Mathematical and numerical foundations of the pseudopotential method

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Fondements mathématiques et numériques de la méthode des pseudopotentiels

Résumé: *Les contributions de cette thèse consistent en trois principaux résultats.*

Le premier résultat concerne la théorie des perturbations analytique pour les modèles de type Kohn-Sham. Nous montrons, sous certaines conditions techniques, l'existence, l'unicité et l' analyticité de la matrice densité de l'état fondamental du modèle de Hartree-Fock réduit pour des perturbations régulières provenant d'un potentiel extérieur. Notre analyse englobe le cas où le niveau de Fermi de l'état fondamental non-perturbé est une valeur propre dégénérée de l'opérateur de champ moyen et où les orbitales frontières sont partiellement occupées.

Le deuxième résultat concerne la construction mathématique de pseudopotentiels pour les modèles Kohn-Sham. Nous définissons l'ensemble des pseudopotentiels semi-locaux à normes conservées de régularité de Sobolev donnée, et nous prouvons que cet ensemble est non-vide et fermé pour une topologie appropriée. Cela nous permet de proposer une nouvelle façon de construire des pseudopotentiels, qui consiste à optimiser sur cet ensemble un critère tenant compte des impératifs de régularité et de transférabilité.

Le troisième résultat est une étude numérique du modèle de Hartree-Fock réduit pour les atomes. Nous proposons une méthode de discrétisation et un algorithme de résolution numérique des équations de Kohn-Sham pour un atome soumis à un potentiel extérieur à symétrie cylindrique. Nous calculons les niveaux d'énergie occupés et les nombres d'occupations pour tous les éléments des quatre premières rangées du tableau périodique et considérons le cas d'un atome soumis à un champ électrique uniforme.

Mathematical and numerical foundations of the pseudopotential method

Abstract: *The contributions of this thesis consist of three main results.*

The first result is concerned with analytic perturbation theory for Kohn-Sham type models. We prove, under some technical conditions, the existence, uniqueness and analyticity of the perturbed reduced Hartree-Fock ground state density matrix for regular perturbations arising from an external potential. Our analysis encompasses the case when the Fermi level of the unperturbed ground state is a degenerate eigenvalue of the mean-field operator and the frontier orbitals are partially occupied.

The second result is concerned with the mathematical construction of pseudopotentials for Kohn-Sham models. We define a set of admissible semilocal norm-conserving pseudopotentials of given local Sobolev regularity and prove that this set is non-empty and closed for an appropriate topology. This allows us to propose a new way to construct pseudopotentials, which consists in optimizing on the latter set some criterion taking into account both smoothness and transferability requirements.

The third result is a numerical study of the reduced Hartree-Fock model of atoms. We propose a discretization method and an algorithm to solve numerically the Kohn-Sham equations for an atom subjected to a cylindrically-symmetric external potential. We report

the computed occupied energy levels and the occupation numbers for all the atoms of the four first rows of the periodic table and consider the case of an atom subjected to a uniform electric-field.

Publications and preprints

- E. Cancès and N. Mourad, *A mathematical perspective on density functional perturbation theory*, Nonlinearity 27 (2014) 1999–2033.
- E. Cancès and N. Mourad, *Existence of optimal norm-conserving pseudopotentials for Kohn-Sham models*, preprint hal-01139375 (2015), submitted.
- E. Cancès and N. Mourad, *A numerical study of the Kohn-Sham ground states of atoms*, in preparation.

Preface (Fr)

L'objectif du premier chapitre est de donner un aperçu de la théorie de la fonctionnelle de la densité et de la théorie des perturbations pour les opérateurs auto-adjoints, ainsi qu'un résumé des résultats nouveaux présentés dans cette thèse.

Les résultats obtenus au cours de ce travail de thèse sont rassemblés dans les trois chapitres suivants:

Chapitre 2. Un point de vue mathématique sur la DFPT (*Density Functional Perturbation Theory*)

Le contenu de ce chapitre reprend un article publié dans *Nonlinearity* [23], complété par une annexe sur la théorie des perturbations au deuxième ordre. L'article est consacré à l'application de la méthode des perturbations analytiques à la théorie de la fonctionnelle de la densité. Nous introduisons d'abord le modèle de Hartree-Fock réduit et expliquons la distinction entre le cas non-dégénéré et le cas dégénéré. Nous établissons également des conditions suffisantes assurant l'unicité de la matrice de densité de l'état fondamental non perturbé de référence. Ensuite, un potentiel de perturbation est ajouté à la fonctionnelle d'énergie. L'objectif de cette contribution est de comprendre l'influence de ce potentiel sur l'énergie et sur la matrice densité de l'état fondamental. Les résultats de base dans le cas non-dégénéré sont rappelés, principalement l'existence, l'unicité et l'analyticité de la matrice densité perturbée par rapport à la perturbation. En outre, nous donnons une formule de récurrence permettant de calculer les coefficients du développement en perturbation. Le cœur de cet article est l'extension de ces résultats au cas dégénéré. Sous certaines hypothèses, nous prouvons des résultats similaires à ceux établis dans le cas non-dégénéré : la matrice densité de l'état fondamental perturbé existe, est unique et est analytique en la perturbation. En outre, une formule de récurrence permet de calculer les coefficients de la série de Rayleigh-Schrödinger. L'approche décrite dans ce chapitre peut être appliquée à d'autres modèles quantiques de champ moyen, comme le modèle de Kohn-Sham LDA (sous certaines hypothèses supplémentaires). Enfin, des démonstrations rigoureuses de la règle $(2n + 1)$ de Wigner sont fournies.

Chapitre 3. Existence de pseudopotentiels à normes conservées optimaux pour le modèle de Kohn-Sham

Ce chapitre traite de la construction mathématique de pseudopotentiels pour le calcul de structures électroniques. Nous rappelons pour commencer la structure et les propriétés de base du modèle de Kohn-Sham pour un atome, d'abord pour un potentiel tous-électrons, puis pour des pseudopotentiels à normes conservées. L'Hamiltonien de champ moyen de l'état fondamental de l'atome est invariant par rotation et ses fonctions propres ont donc des propriétés spécifiques, que nous étudions en détail car elles jouent un rôle important dans la théorie du pseudopotentiel. Nous décrivons la façon de construire des pseudopotentiels à normes conservées et nous définissons l'ensemble des pseudopotentiels semi-locaux è normes conservées admissibles. Nous montrons que, pour le modèle de Hartree (également appelé modèle de Hartree-Fock réduit), cet ensemble est non-vide et fermé pour une topologie appropriée. Nous démontrons également quelques résultats de stabilité du

modèle de Hartree avec pseudopotentiel, par rapport aux perturbations extérieures et aux variations du pseudopotentiel lui-même. Nous étendons ensuite quelques-uns des résultats obtenus au Chapitre 2 dans le cadre de la théorie des perturbations régulières au cas d'une perturbation par un champ électrique uniforme (potentiel de Stark). Nous construisons en particulier la perturbation au premier ordre de la matrice densité à la fois pour le modèle tous-électrons et pour le modèle avec pseudopotentiel. Nous proposons enfin une nouvelle façon de construire des pseudopotentiels consistant à choisir le "meilleur" pseudopotentiel selon un certain critère d'optimalité, et nous montrons l'existence d'un pseudopotentiel optimal pour divers critères d'optimalité (certains d'entre eux impliquant la réponse linéaire de la densité atomique de l'état fondamental à des potentiels de Stark). Enfin, nous discutons des extensions possibles de nos résultats au modèle de Kohn-Sham LDA. Ce travail a fait l'objet d'une pré-publication [25] et a été soumis pour publication.

Chapitre 4. Une étude numérique du modèle de Kohn-Sham pour les atomes

Ce chapitre traite de la simulation numérique du modèle de Kohn-Sham pour les atomes soumis à des potentiels extérieurs à symétrie cylindrique. Nous traitons à la fois le modèle de Hartree et le modèle Xα. Nous commençons par présenter ces modèles avec et sans perturbation et par rappeler quelques résultats théoriques bien connus dont nous avons besoin. L'approximation variationnelle du modèle et la construction d'espaces de discrétisation appropriés (en utilisant les éléments finis $\mathbb{P}_4$) sont détaillées, ainsi que l'algorithme pour résoudre les équations de Kohn-Sham discrétisées utilisé dans notre code. La dernière section est consacrée aux résultats numériques que nous avons obtenus : d'abord, nous présentons les niveaux d'énergie calculés de tous les atomes des quatre premières lignes du tableau périodique. Fait intéressant, nous observons dégénérescences accidentelles entre des couches s et d ou p et d au niveau de Fermi de quelques atomes. Ensuite, nous considérons le cas d'un atome soumis à un champ électrique uniforme. On trace la réponse de la densité de l'atome de bore pour différentes amplitudes du champ électrique, calculée numériquement dans une grande boule avec des conditions aux limites de Dirichlet, et on vérifie que, dans la limite de petits champs électriques, cette réponse est équivalente à la perturbation au premier ordre de la densité de l'état fondamental. Quelques détails techniques sont rassemblés dans une annexe à la fin du chapitre.

Contents

Chapter 1

Introduction and summary of results

The aim of this chapter is to give a brief overview of the density functional theory and of the perturbation theory for self-adjoint operators, as well as a summary of the new results presented in this thesis.

Several models are used to describe the electronic structure of atoms and molecules. The electronic Schrödinger equation is a very accurate ab-initio model, but unfortunately, it is difficult to deal with it numerically, since it is a high-dimensional partial differential equation. Nonlinear mean-field models, which are approximations of the electronic Schrödinger equation, are on the other hand widely used in computational physics and chemistry. The most commonly used among these models are the Hartree Fock (HF) and Kohn-Sham (KS) models. The HF model is a variational approximation of the electronic Schrödinger equation. An introduction to density functional theory (DFT) and the Kohn-Sham models is given in Section 1.1.

Perturbation theory (PT) is an important tool in quantum chemistry. One of its application is that it can be used to compute the response properties of molecular systems to external electromagnetic fields. In Section 1.2, the main results of the perturbation theory for linear self-adjoint operators in both degenerate and non-degenerate cases are recalled. Perturbation methods for some nonlinear mean-field models [21] are dealt with in Chapter 2.

The contributions of this thesis are summarized in Section 1.3. First, we describe the results on density functional perturbation theory clarified in Chapter 2 and published in [23]. Second, we give an overview of our study of the pseudopotential method presented in Chapter 3. Finally, we summarize the numerical results presented in Chapter 4.

1.1 Mathematical modeling of molecular systems

Density functional theory is the most widely used approach in ground state electronic structure calculations. The purpose of this section is to give an introduction to DFT. We explain in particular how it is derived from the many-body Schrödinger equation describing a finite molecular system.

1.1.1 Many-body Schrödinger equation

A non-relativistic isolated quantum system consisting of N particles can be modeled by a separable complex Hilbert space $\mathcal{H}$, called the state space, and a self-adjoint operator on $\mathcal{H}$, denoted by H, called the Hamiltonian. The time-dependent Schrödinger equation has the form

$$i\hbar\frac{d\Psi}{dt}(t) = H\Psi(t), \tag{1.1}$$

where $\hbar$ is the reduced Planck constant. The wave function $\Psi(t)$ is a normalized vector in $\mathcal{H}$. It is the object which completely describes the state of the quantum system at time t.

Equation (1.1) is a first order linear evolution equation. The stationary states are of special interest. They have the form $\Psi(t) = e^{i\alpha(t)}\psi$, where $\|\psi\|_{\mathcal{H}} = 1$ and $\alpha(t) = -iEt/\hbar$. Inserting $\Psi(t)$ in equation (1.1), one gets that the function ψ satisfies the time-independent Schrödinger equation

$$H\psi = E\psi. \tag{1.2}$$

The number E is from a physical point of view the energy of the state ψ.

The state space associated to a one-particle system with spin s is $\mathcal{H} = L^2(\mathbb{R}^3 \times \Sigma, \mathbb{C})$, where Σ is a discrete set of cardinality $2s+1$. For a system consisting of N-particles, the state space is a subspace of the tensor product of the N one-particle state spaces. For simplicity, let us first consider two particles with spins s_1 and s_2. If the two particles are of different nature then the state space of the two-particle system is $L^2(\mathbb{R}^3 \times \Sigma_1, \mathbb{C}) \otimes L^2(\mathbb{R}^3 \times \Sigma_2, \mathbb{C}) \equiv L^2(\mathbb{R}^6, \mathbb{C}^{(2s_1+1)(2s_2+1)})$. If the two particles are identical we get:

- for bosons, the state space is the *symmetrized* tensor product of the one-particle state space, denoted by $L^2(\mathbb{R}^3 \times \Sigma, \mathbb{C}) \vee L^2(\mathbb{R}^3 \times \Sigma, \mathbb{C})$, where $\Sigma = \Sigma_1 = \Sigma_2$,
- for fermions, the state space is the *antisymmetrized* tensor product of the one-particle state space, denoted by $L^2(\mathbb{R}^3 \times \Sigma, \mathbb{C}) \wedge L^2(\mathbb{R}^3 \times \Sigma, \mathbb{C})$.

More explicitly, the wave function Ψ satisfies the following symmetry properties: for all $(\mathbf{r}_1, \sigma_1; \mathbf{r}_2, \sigma_2) \in \mathbb{R}^3 \times \Sigma \times \mathbb{R}^2 \times \Sigma$,

$$\begin{aligned}
\Psi(t; \mathbf{r}_2, \sigma_2; \mathbf{r}_1, \sigma_1) &= \Psi(t; \mathbf{r}_1, \sigma_1; \mathbf{r}_2, \sigma_2) \qquad \text{(for two identical bosons)},\\
\Psi(t; \mathbf{r}_2, \sigma_2; \mathbf{r}_1, \sigma_1) &= -\Psi(t; \mathbf{r}_1, \sigma_1; \mathbf{r}_2, \sigma_2) \quad \text{(for two identical fermions)}.
\end{aligned}$$

Consider now the general case of N-particles, where the i-th particle has a mass m_i and is subjected to an external potential V_{ext} and where the interaction between the i-th and the j-th particles is described by the two-body potential W_{ij}. The quantity $|\Psi(t; \mathbf{r}_1, \sigma_1; \cdots; \mathbf{r}_N, \sigma_N)|^2$ can be interpreted as the probability density of observing at time t, the first particle at position $\mathbf{r}_1 \in \mathbb{R}^3$ with spin σ_1, the second particle at position $\mathbf{r}_2$ with spin σ_2, etc. The Hamiltonian H is the equal to

$$H = -\sum_{i=1}^{N} \frac{\hbar^2}{2m_i}\Delta_{\mathbf{r}_i} + \sum_{i=1}^{N} V_{\text{ext}}(\mathbf{r}_i) + \sum_{1 \le i < j \le N} W_{ij}(\mathbf{r}_i, \mathbf{r}_j).$$

In the sequel the spin variable is omitted for simplicity.

1.1.2 Quantum description of a molecular system

In the sequel, we will work with the atomic units, so that

$$\hbar = 1, \quad m_e = 1, \quad e = 1, \quad 4\pi\epsilon_0 = 1,$$

where m_e is the electron mass, e is the elementary charge and ϵ_0 is the dielectric permittivity of the vacuum.

Consider an isolated molecule composed of M nuclei and N electrons. Denote by

$$\mathcal{H}_N := \wedge^N L^2(\mathbb{R}^3),$$

the subspace of the N-tensor product of $L^2(\mathbb{R}^3)$, consisting of antisymmetric functions. A time-dependent molecular wavefunction is, in the position representation, a function $\Psi(t, \mathbf{R}_1, \cdots, \mathbf{R}_M; \mathbf{r}_1, \cdots, \mathbf{r}_N)$ and belongs to $L^2(\mathbb{R}^{3M}) \otimes \mathcal{H}_N$. The Hamiltonian of this molecular system is

$$\begin{aligned} H_{\text{mol}} = \quad & -\sum_{k=1}^{M} \tfrac{1}{2m_k} \Delta_{\mathbf{R}_k} - \sum_{i=1}^{N} \tfrac{1}{2} \Delta_{\mathbf{r}_i} - \sum_{i=1}^{N} \sum_{k=1}^{M} \tfrac{z_k}{|\mathbf{r}_i - \mathbf{R}_k|} \\ & + \sum_{1 \le i < j \le N} \tfrac{1}{|\mathbf{r}_i - \mathbf{r}_j|} + \sum_{1 \le k < l \le M} \tfrac{z_k z_l}{|\mathbf{R}_k - \mathbf{R}_l|}, \end{aligned} \tag{1.3}$$

where m_k and z_k are the mass and the electric charge of the k-th nucleus, respectively. The first two terms in H_{mol} correspond to the kinetic energy of the nuclei and the electrons, respectively. The later three terms correspond to the electrostatic energy of the interaction between electrons and nuclei, between electrons, and between nuclei, respectively.

It is to be remarked that this model does not depend on empirical parameters specific to the molecular system. It only depends on fundamental constants of physics, of the number of electrons, and of the masses and charges of the nuclei. On the other hand, it is difficult to use it to compute the properties of the molecular system, as it requires solving a $3(M + N)$-dimensional partial differential equation. In practice, this becomes hard as long as $M + N > 3$.

1.1.3 Born-Oppenheimer approximation

Since the nuclei are much heavier than the electrons, the mass ratio m_e/m_n is a small parameter, and it is possible to decouple the nuclear and electronic degrees of freedom by means of an adiabatic limit [62]. It can then be shown that, in most cases, nuclei behave as classical point-like particles interacting through an effective potential energy function $W : \mathbb{R}^{3M} \to \mathbb{R}$,

$$W(\mathbf{R}_1, \cdots, \mathbf{R}_M) = I(\mathbf{R}_1, \cdots, \mathbf{R}_k) + \sum_{1 \le k < l \le M} \frac{z_k z_l}{|\mathbf{R}_k - \mathbf{R}_l|}, \tag{1.4}$$

where $I(\mathbf{R}_1, \cdots, \mathbf{R}_k)$ is the effective potential created by the electrons and where the second term in (1.4) is due to the repulsive Coulomb forces between the nuclei. In fact, the value of $I(\mathbf{R}_1, \cdots, \mathbf{R}_k)$ is the ground state energy of the electronic Hamiltonian

$$H_{\text{elec}}^{\{\mathbf{R}_k\}} = -\frac{1}{2} \sum_{i=1}^{N} \Delta_{\mathbf{r}_i} - \sum_{i=1}^{N} \sum_{k=1}^{M} \frac{z_k}{|\mathbf{r}_i - \mathbf{R}_k|} + \sum_{1 \le i < j \le N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|},$$

which is a self-adjoint operator on $\mathcal{H}_N = \wedge^N L^2(\mathbb{R}^3)$, parametrized by the nuclear positions. It can be obtained by solving the following minimization problem

$$I(\mathbf{R}_1, \cdots, \mathbf{R}_k) = \inf \left\{ \langle \Psi | H_{\rm elec}^{\{\mathbf{R}_k\}} | \Psi \rangle, \ \Psi \in \mathcal{Q}_N, \ \|\Psi\|_{\mathcal{H}_N} = 1 \right\}, \tag{1.5}$$

where

$$\mathcal{Q}_N = \mathcal{H}_N \cap H^1(\mathbb{R}^3)$$

is the form domain of the electronic Hamiltonian $H_{\rm elec}^{\{\mathbf{R}_k\}}$. Note that to solve (1.5), it suffices to minimize on real-valued wavefunctions. We therefore considered here $\mathcal{Q}_N$ as a space of real-valued functions. In what follows, we will focus on the electronic problem (1.5) for a given configuration $\{\mathbf{R}_k\}$ of the nuclei. For simplicity we will denote by

$$E_0 := I(\mathbf{R}_1, \cdots, \mathbf{R}_k) \quad \text{and} \quad H_N := H_{\rm elec}^{\{\mathbf{R}_k\}},$$

so that

$$H_N = -\frac{1}{2} \sum_{i=1}^N \Delta_{\mathbf{r}_i} + \sum_{i=1}^N V_{\rm ne}(\mathbf{r}_i) + \sum_{1 \leq i < j \leq N} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

with

$$V_{\rm ne}(\mathbf{r}) = -\sum_{k=1}^M \frac{z_k}{|\mathbf{r} - \mathbf{R}_k|},$$

and

$$E_0 = \inf \left\{ \langle \Psi | H_N | \Psi \rangle, \ \Psi \in \mathcal{X}_N \right\}, \tag{1.6}$$

where

$$\mathcal{X}_N = \{ \Psi \in \mathcal{Q}_N, \ \|\Psi\|_{\mathcal{H}_N} = 1 \}$$

is the set of admissible wavefunctions.

The operator H_N is always bounded below, and its essential spectrum is a half-line: $\sigma_{\rm ess}(H_N) = [\Xi^N, +\infty[$. For neutral or positively charged molecules, H_N possesses infinitely many discrete eigenvalues below $\Xi^N := \min \sigma_{\rm ess}(H_N)$. For $N = 1$, we have $\Xi^1 = 0$, and for $N \geq 2$, Ξ^N is equal to the ground state energy of H_{N-1} (see figure 1.1). This is a special case of the HVZ theorem (see e.g. [69, p.120, 343] and [97]), which was proved by Hunziker [45], van Winter [95] and Zhislin [96].

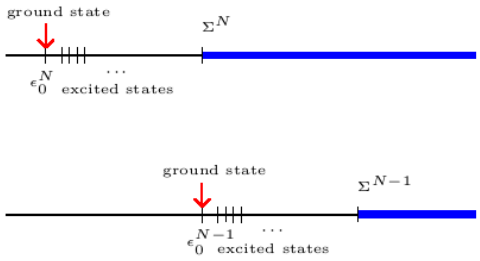

Figure 1.1 – The graphs of the spectra of H^N and H^{N-1} respectively (*HVZ-theorem*).

Even though applying the Born-Oppenheimer approximation simplifies the original fully quantum problem, solving (1.6) for N large remains extremely difficult. Nonlinear mean-field models such as Hartree-Fock and Kohn-Sham models provide relatively accurate approximations of (1.6) at a reasonable computational cost.

It should be noted that the Born-Oppenheimer approximation does not account for correlated dynamics of ions and electrons, such that polaron-induced superconductivity, or some diffusion phenomena in solids. See [14, 31] for mathematical studies of cases when this approximation breaks down.

1.1.4 Density functional theory

The idea of the density functional theory (DFT) is to replace the minimization (1.6) over admissible wavefunctions by a minimization over the set of admissible electronic densities. Let us recall that the density associated with a wavefunction $\Psi \in \mathcal{H}_N$ is defined by

$$\rho_\Psi(\mathbf{r}) := N \int_{\mathbb{R}^{3(N-1)}} |\Psi(\mathbf{r}, \mathbf{r}_2, \cdots, \mathbf{r}_N)|^2 \, d\mathbf{r}_2 \cdots d\mathbf{r}_N. \tag{1.7}$$

Density functional theory was introduced first by Hohenberg and Kohn [53] and Kohn and Sham [51], and formalized by Levy [54], Valone [89, 90] and Lieb [55]. The first step consists in writing the electronic Hamiltonian as

$$H_N = H_N^1 + \sum_{i=1}^N V_{\rm ne}(\mathbf{r}_i) \quad \text{with} \quad H_N^\lambda = -\frac{1}{2}\sum_{i=1}^N \Delta_{\mathbf{r}_i} + \sum_{1\le i<j\le N} \frac{\lambda}{|\mathbf{r}_i - \mathbf{r}_j|}. \tag{1.8}$$

The operator H_N^1 is generic and only depends on the number N of the electrons in the system, while $V_{\rm ne}$ is specific, in the sense that it depends on the molecular system under consideration. Note that, for any $\Psi \in \mathcal{X}_N$, we have

$$\begin{aligned}\langle\Psi| \sum_{i=1}^N V_{\rm ne}(\mathbf{r}_i) |\Psi\rangle = \sum_{i=1}^N \int_{\mathbb{R}^{3N}} V_{\rm ne}(\mathbf{r}_i) |\Psi(\mathbf{r}_1, \cdots, \mathbf{r}_N)|^2 \, d\mathbf{r}_1 \cdots d\mathbf{r}_N \\ = \int_{\mathbb{R}^3} \rho_\Psi V_{\rm ne}. \end{aligned} \tag{1.9}$$

Define the set of the admissible electronic densities

$$\mathcal{R}_N = \left\{\rho \mid \exists \Psi \in \mathcal{X}_N \text{ s.t. } \rho_\Psi = \rho\right\}.$$

It is proved in [55] that

$$\mathcal{R}_N = \left\{\rho \geq 0 \mid \sqrt{\rho} \in H^1(\mathbb{R}^3),\ \int_{\mathbb{R}^3} \rho = N\right\}.$$

Using (1.8) and (1.9), problem (1.6) is equivalent to

$$E_0 \ = \ \inf\left\{\langle\Psi|H_N^1|\Psi\rangle + \textstyle\int_{\mathbb{R}^3} \rho_\Psi V_{\rm ne},\ \Psi \in \mathcal{X}_N\right\}.$$

An elementary calculation shows that

$$E_0 = \inf \left\{ F_N^{\mathrm{LL}}(\rho) + \int_{\mathbb{R}^3} \rho V_{\mathrm{ne}},\ \rho \in \mathcal{R}_N \right\}, \tag{1.10}$$

where F_N^{LL} is the Levy-Lieb functional defined by

$$F_N^{\mathrm{LL}}(\rho) = \inf \left\{ \langle \Psi | H_N^1 | \Psi \rangle,\ \Psi \in \mathcal{X}_N,\ \rho_\Psi = \rho \right\}. \tag{1.11}$$

It is a universal density functional, in the sense that it does not depend on the considered molecular system. It only depends on the number of electrons.

The states that can be described by a single wave function $\Psi \in \mathcal{X}_N$ are called *pure states*. The N-body density operator associated with Ψ is the operator Γ_Ψ on $\mathcal{H}_N$ defined by

$$\Gamma_\Psi := |\Psi\rangle\langle\Psi|.$$

By definition, the density associated with Γ_Ψ is the density associated with the wave function Ψ, that is

$$\rho_{\Gamma_\Psi}(\mathbf{r}) = \rho_\Psi(\mathbf{r}) = N \int_{\mathbb{R}^{3(N-1)}} |\Psi(\mathbf{r}, \mathbf{r}_2, \cdots, \mathbf{r}_N)|^2 \, d\mathbf{r}_2 \cdots d\mathbf{r}_N. \tag{1.12}$$

The one-body reduced density matrix associated with Ψ is the operator γ_Ψ on $L^2(\mathbb{R}^3)$ defined by the integral kernel

$$\gamma_\Psi(\mathbf{r}, \mathbf{r}') := N \int_{\mathbb{R}^{3(N-1)}} \Psi(\mathbf{r}, \mathbf{r}_2, \cdots, \mathbf{r}_N) \Psi(\mathbf{r}', \mathbf{r}_2, \cdots, \mathbf{r}_N) \, d\mathbf{r}_2 \cdots d\mathbf{r}_N. \tag{1.13}$$

Recall that we only deal with real-valued wavefunctions Ψ. In fact, not all molecular states can be described by a single wavefunction. This is the case of *mixed states*, which are fundamental objects in statistical physics, and are convex combinations of the pure states. A mixed state can be described by a N-body density operator

$$\Gamma = \sum_{i=1}^{\infty} p_i |\Psi_i\rangle\langle\Psi_i|; \quad 0 \le p_i \le 1, \quad \sum_{i=1}^{\infty} p_i = 1, \quad \Psi_i \in \mathcal{X}_N; \quad i \in \mathbb{N}^*. \tag{1.14}$$

From a physical point of view, the coefficient p_i is the probability for the system to be in the pure state Ψ_i. The density and the one-body reduced density matrix associated to the N-body density operator Γ defined by (1.14) are respectively defined by

$$\rho_\Gamma(\mathbf{r}) = \sum_{i=1}^{\infty} p_i \rho_{\Psi_i}(\mathbf{r})$$

and

$$\gamma_\Gamma = \sum_{i=1}^{\infty} p_i \gamma_{\Psi_i}, \tag{1.15}$$

where ρ_{Ψ_i} and γ_{Ψ_i} are defined by (1.12) and (1.13), respectively. An important point to be mentioned is that the mappings $\Gamma \mapsto \rho_\Gamma$ and $\Gamma \mapsto \gamma_\Gamma$ are linear. Denote by

$$\mathcal{D}_N = \{\Gamma \in \mathcal{S}(\mathcal{H}_N) | \quad 0 \le \Gamma \le 1, \quad \mathrm{Tr}\,(\Gamma) = 1, \quad \mathrm{Tr}\,(-\Delta\Gamma) < \infty\},$$

where $\mathcal{S}(\mathcal{H}_N)$ is the space of bounded self-adjoint operators on $\mathcal{H}_N$, $0 \leq \Gamma \leq 1$ means $0 \leq \langle \Gamma\Psi, \Psi\rangle \leq 1$, for any Ψ in $\mathcal{H}_N$, and $\mathrm{Tr}\,(-\Delta\Gamma) = \mathrm{Tr}\,(|\nabla|\Gamma|\nabla|)$. In fact, the set $\mathcal{D}_N$ is the convex hull of the set of the density operators associated with pure states. It can be checked that

$$\mathrm{Tr}\,(H_N\Gamma) = \mathrm{Tr}\,(H_N^1\Gamma) + \int_{\mathbb{R}^3} \rho_\Gamma V_{\mathrm{ne}}$$

and

$$\begin{aligned}\mathcal{R}_N &= \{\rho \mid \exists \Psi \in \mathcal{X}_N \text{ s.t. } \rho_\Psi = \rho\} \\ &= \{\rho \mid \exists \Gamma \in \mathcal{D}_N \text{ s.t. } \rho_\Gamma = \rho\} \\ &= \left\{\rho \geq 0 \mid \sqrt{\rho} \in H^1(\mathbb{R}^3),\ \int_{\mathbb{R}^3} \rho = N\right\}.\end{aligned}$$

The above results are known as the N-representability of densities. As

$$\begin{aligned}E_0 &= \inf\left\{\langle\Psi|H_N|\Psi\rangle;\ \Psi \in \mathcal{X}_N\right\} \\ &= \inf\left\{\mathrm{Tr}\,(H_N\Gamma_\psi);\ \Psi \in \mathcal{X}_N\right\} \\ &= \inf\left\{\mathrm{Tr}\,(H_N\Gamma);\ \Gamma \in \mathcal{D}_N\right\},\end{aligned}$$

we get, with the help of (1.8) and (1.9),

$$E_0 = \inf\left\{F_N^{\mathrm{L}}(\rho) + \int_{\mathbb{R}^3} \rho V_{\mathrm{ne}},\ \rho \in \mathcal{R}_N\right\}, \tag{1.16}$$

where F_N^{L} is the Lieb functional, defined by

$$F_N^{\mathrm{L}}(\rho) = \inf\left\{\mathrm{Tr}\,(H_N^1\Gamma),\ \Gamma \in \mathcal{D}_N,\ \rho_\Gamma = \rho\right\}.$$

Formulation (1.16) is more satisfactory than (1.10) from a mathematical point of view, as it is a convex problem.

We have thus formulated the ground state electronic problem, as a function of the density. Unfortunately, there is no simple way to evaluate F_N^{L} and F_N^{LL}.

1.1.5 Thomas-Fermi and related models

The idea underlying the Thomas-Fermi model [32, 84] (1927) is to approximate

- the electronic kinetic energy by $C_{\mathrm{TF}} \int_{\mathbb{R}^3} \rho(x)^{\frac{5}{3}} dx$. This approximation is based on the fact that the kinetic energy density of a homogeneous gas of non-interacting electrons with density ρ is equal to $C_{\mathrm{TF}}\rho^{\frac{5}{3}}$, where

  $$C_{\mathrm{TF}} = \frac{10}{3}(3\pi^2)^{\frac{2}{3}}$$

  is the Thomas-Fermi constant;

- the electron repulsion energy by $\frac{1}{2}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3} \frac{\rho(x)\rho(y)}{|x-y|}\, dx\, dy$, which is the electrostatic energy of a classical charge distribution of density ρ.

The Thomas-Fermi (TF) energy functional, then reads

$$F_{\mathrm{TF}}(\rho) = C_{\mathrm{TF}} \int_{\mathbb{R}^3} \rho^{5/3} + \frac{1}{2} \iint_{\mathbb{R}^3 \times \mathbb{R}^3} \frac{\rho(x)\rho(y)}{|x-y|}\, dx\, dy.$$

In the Thomas-Fermi-von Weizsäcker (TFW) model, the term $C_{\mathrm{W}} \int_{\mathbb{R}^3} |\nabla \sqrt{\rho}|^2$ is added as a correction to the TF approximation of the kinetic energy to account for the non-uniformity of electron densities in molecular system [92]. The TFW energy functional thus reads

$$F_{\mathrm{TFW}}(\rho) = C_{\mathrm{W}} \int_{\mathbb{R}^3} |\nabla \sqrt{\rho}|^2 + C_{\mathrm{TF}} \int_{\mathbb{R}^3} \rho^{5/3} + \frac{1}{2} \iint_{\mathbb{R}^3 \times \mathbb{R}^3} \frac{\rho(x)\rho(y)}{|x-y|}\, dx\, dy,$$

where C_{W} takes different values depending on how the correction is derived [28].

In the Thomas-Fermi-Dirac-von Weizsäcker (TFDW) model, a term of the form $-C_{\mathrm{D}} \int_{\mathbb{R}^3} \rho^{\frac{4}{3}}$ is added to the TFW, where

$$C_{\mathrm{D}} = \frac{3}{4}\left(\frac{3}{\pi}\right)^{\frac{1}{3}}$$

is the Dirac constant, to deal with exchange effects. The TFDW energy functional reads

$$\begin{aligned} F_{\mathrm{TFDW}}(\rho) = C_{\mathrm{W}} \int_{\mathbb{R}^3} |\nabla \sqrt{\rho}|^2 - C_{\mathrm{D}} \int_{\mathbb{R}^3} \rho^{\frac{4}{3}} + C_{\mathrm{TF}} \int_{\mathbb{R}^3} \rho^{5/3} \\ + \frac{1}{2} \iint_{\mathbb{R}^3 \times \mathbb{R}^3} \frac{\rho(x)\rho(y)}{|x-y|}\, dx\, dy. \end{aligned}$$

The minimization problem of the Thomas-Fermi type models has the form

$$E_0^{\mathrm{TF,TFW,TFDW}} = \inf \left\{ F_{\mathrm{TF,TFW,TFDW}}(\rho) + \int_{\mathbb{R}^3} \rho V_{\mathrm{ne}},\ \rho \in \mathcal{R}_N \right\},$$

where $F_{\mathrm{TF,TFW,TFDW}}$ is one of the above defined energy functionals.

It is to be remarked that Thomas-Fermi energy functionals are explicit functionals of the density. They belong to the class of orbital-free models, in contrast with the Kohn-Sham models, in which the energy functional is expressed in terms of one-electron Kohn-Sham orbitals and associated occupation numbers, or equivalently in terms of one-body reduced density matrix. Thomas-Fermi models are not used much anymore in chemistry and physics, but they are still of interest from a mathematical point of view, since they are used to test mathematical techniques.

1.1.6 Kohn-Sham models

The Kohn-Sham method [51], introduced in 1965, is currently the mostly used approach for electronic structure calculation in materials science, quantum chemistry and condensed matter physics, as it provides the best compromise between computational efficiency and accuracy. This method proceeds from DFT as follows:

- the kinetic energy is approximated by the kinetic energy of a system of N non-interacting electrons. We then obtain for the pure states

$$\tilde{T}_{\mathrm{KS}}(\rho) = \inf\left\{\langle\Psi|H_N^0|\Psi\rangle,\ \Psi\in\mathcal{X}_N,\ \rho_\Psi=\rho\right\}, \tag{1.17}$$

  and for the mixed states

$$T_{\mathrm{J}}(\rho) = \inf\left\{\mathrm{Tr}\,(H_N^0\Gamma),\ \Gamma\in\mathcal{D}_N,\ \rho_\Gamma=\rho\right\}. \tag{1.18}$$

  The functional T_{J} is called the Janack kinetic energy functional;

- the repulsion energy between electrons is approximated by the classical Coulomb electrostatic energy

$$J(\rho) = \frac{1}{2}\iint_{\mathbb{R}^3\times\mathbb{R}^3}\frac{\rho(x)\rho(y)}{|x-y|}\,dx\,dy;$$

- the errors on the kinetic energy and the electron repulsion energy are put together in a single term, called the exchange-correlation functional, defined by the difference

$$E_{\mathrm{xc}}(\rho) = F_N^{\mathrm{LL}}(\rho) - \tilde{T}_{\mathrm{KS}}(\rho) - J(\rho)$$

  or

$$E_{\mathrm{xc}}(\rho) = F_N^{\mathrm{L}}(\rho) - T_{\mathrm{J}}(\rho) - J(\rho),$$

  depending on the choice of whether working with the pure or mixed states. It is numerically shown that the exchange-correlation energy is about 10% of the total energy.

The Janack kinetic energy defined by (1.18) can be rewritten as a functional of the one-body reduced density matrix γ_Γ defined by (1.15). Indeed

$$\mathrm{Tr}\,(H_N^0\Gamma) = \mathrm{Tr}\,(-\frac{1}{2}\Delta\gamma_\Gamma)$$

and

$$\{\gamma|\ \exists\,\Gamma\in\mathcal{D}_N,\ \gamma_\Gamma=\gamma\} = \mathcal{K}_N,$$

where

$$\mathcal{K}_N = \left\{\gamma\in\mathcal{S}(L^2(\mathbb{R}^3))|\ 0\le\gamma\le 1,\ \mathrm{Tr}\,(\gamma)=N,\ \mathrm{Tr}\,(-\Delta\gamma)<\infty\right\}. \tag{1.19}$$

The above result is known as the mixed-state N-representability of one-body reduced density matrices (1-RDM). Thus the Janack kinetic energy is equal to

$$T_{\mathrm{J}}(\rho) = \inf\left\{\mathrm{Tr}\,(-\frac{1}{2}\Delta\gamma),\ \gamma\in\mathcal{K}_N,\ \rho_\gamma=\rho\right\}.$$

Note that any $\gamma\in\mathcal{K}_N$ can be written as

$$\gamma = \sum_{i=1}^{\infty} n_i|\phi_i\rangle\langle\phi_i|,$$

with

$$\phi_i \in H^1(\mathbb{R}^3), \quad \int_{\mathbb{R}^3} \phi_i\phi_j = \delta_{ij}, \quad n_i \in [0,1], \quad \sum_{i=1}^{\infty} n_i = N,$$
$$\text{and} \quad \sum_{i=1}^{\infty} n_i \|\nabla\phi_i\|^2_{L^2(\mathbb{R}^3)} < \infty.$$

In particular, the density associated with $\gamma \in \mathcal{K}_N$ is

$$\rho_\gamma(\mathbf{r}) = \sum_{i=1}^{\infty} n_i |\phi_i(\mathbf{r})|^2.$$

Hence, the Janack kinetic energy can be equivalently rewritten as

$$T_{\mathrm{J}}(\rho) = \inf\left\{ \frac{1}{2}\sum_{i=1}^{\infty} n_i \int_{\mathbb{R}^3} |\nabla\phi_i|^2,\ \Phi = (\phi_i)_{i\in\mathbb{N}^*} \in \mathcal{W},\right.$$
$$\left. \nu = (n_i)_{i\in\mathbb{N}^*} \in \mathcal{N}_N,\ \sum_{i=1}^{\infty} n_i|\phi_i|^2 = \rho \right\},$$

where

$$\mathcal{W} := \left\{ \Phi = (\phi_i)_{i\in\mathbb{N}^*},\ \phi_i \in H^1(\mathbb{R}^3),\ \int_{\mathbb{R}^3} \phi_i\phi_j = \delta_{ij} \right\}$$

and

$$\mathcal{N}_N := \left\{ \nu = (n_i)_{i\in\mathbb{N}^*},\ 0 \le n_i \le 1,\ \sum_{i=1}^{\infty} n_i = N \right\}.$$

Unfortunately, no such simple expression for $\tilde{T}_{\mathrm{KS}}(\rho)$ is available. In the standard Kohn-Sham model, it is assumed that a minimizer of (1.17) is a Slater determinant (which is not always the case [55]), so that $\tilde{T}_{\mathrm{KS}}(\rho)$ can be replaced by

$$T_{\mathrm{KS}}(\rho) = \inf\left\{ \frac{1}{2}\sum_{i=1}^{N} \int_{\mathbb{R}^3} |\nabla\phi_i|^2,\ \Phi = (\phi_1, \cdots, \phi_N) \in (H^1(\mathbb{R}^3))^N,\right.$$
$$\left. \int_{\mathbb{R}^3} \phi_i\phi_j = \delta_{ij},\ \rho_\Phi = \sum_{i=1}^{N} |\phi_i|^2 = \rho \right\}.$$

We recall that a Slater determinant is a wave function Ψ of the form

$$\Psi(\mathbf{r}_1, \cdots, \mathbf{r}_N) = \frac{1}{N!}\det(\phi_i(\mathbf{r}_j)), \text{ with } \phi_i \in L^2(\mathbb{R}^3), \text{ and } \int_{\mathbb{R}^3} \phi_i\phi_j = \delta_{ij}.$$

Note that, for any $\rho \in \mathcal{R}_N$, it holds

$$T_{\mathrm{J}}(\rho) \le \tilde{T}_{\mathrm{KS}}(\rho) \le T_{\mathrm{KS}}(\rho).$$

The standard Kohn-Sham model, built from the Levy-Lieb functional, with integer occupation numbers, reads

$$E_0^{\mathrm{KS}} = \inf\left\{ E^{KS}(\Phi),\ \Phi = (\phi_1, \cdots, \phi_N) \in (H^1(\mathbb{R}^3))^N,\ \int_{\mathbb{R}^3} \phi_i\phi_j = \delta_{ij} \right\}, \tag{1.20}$$

with

$$E^{\mathrm{KS}}(\Phi) = \frac{1}{2}\sum_{i=1}^{N}\int_{\mathbb{R}^3}|\nabla\phi_i|^2 + \int_{\mathbb{R}^3}\rho_\Phi V_{\mathrm{ne}} + J(\rho_\Phi) + E_{\mathrm{xc}}(\rho_\Phi).$$

The Kohn-Sham equations obtained from the first-order optimality conditions associated with the constrained optimization problem (1.20) read (after some algebraic manipulation)

$$\begin{cases} \Phi^0 = (\phi_1, \cdots, \phi_N) \in (H^1(\mathbb{R}^3))^N, \\ H^{\mathrm{KS}}_{\Phi^0}\,\phi_i = \varepsilon_i\phi_i, \\ \int_{\mathbb{R}^3}\phi_i\phi_j = \delta_{ij}, \\ H^{\mathrm{KS}}_{\Phi^0} = -\frac{1}{2}\Delta + V_{\mathrm{ne}} + (\rho_{\Phi^0}\star|\cdot|^{-1}) + v^{\mathrm{xc}}(\rho_{\Phi^0}), \end{cases}$$

where $v^{\mathrm{xc}} = \frac{\partial E^{xc}(\rho)}{\partial\rho}$.

The extended Kohn-Sham model, built from the Lieb functional, with possibly fractional occupation numbers, reads

$$E_0^{\mathrm{EKS}} = \inf\left\{E^{EKS}(\gamma),\ \gamma\in\mathcal{K}_N\right\}, \tag{1.21}$$

with

$$E^{\mathrm{EKS}}(\gamma) = \mathrm{Tr}\,(-\frac{1}{2}\Delta\gamma) + \int_{\mathbb{R}^3}\rho_\gamma V_{\mathrm{ne}} + J(\rho_\gamma) + E_{\mathrm{xc}}(\rho_\gamma),$$

which is equivalent to (with slight abuse of notation) the following orbital formulation

$$E_0^{\mathrm{EKS}} = \inf\left\{E^{EKS}(\nu,\Phi),\ \Phi\in\mathcal{W},\ \nu\in\mathcal{N}_N\right\},$$

with

$$E^{\mathrm{EKS}}(\nu,\Phi) = \frac{1}{2}\sum_{i=1}^{\infty}n_i\int_{\mathbb{R}^3}|\nabla\phi_i|^2 + \int_{\mathbb{R}^3}\rho_{\nu,\Phi}V_{\mathrm{ne}} + J(\rho_{\nu,\Phi}) + E_{\mathrm{xc}}(\rho_{\nu,\Phi}),$$

where $\rho_{\nu,\Phi} := \sum_{i=1}^{\infty}n_i|\phi_i|^2$. The Euler-Lagrange equation of problem (1.21) is (after algebraic manipulation)

$$\begin{cases} \Phi = (\phi_i)_{i\in\mathbb{N}^*}\in\mathcal{W},\ \nu = (n_i)_{i\in\mathbb{N}^*}\in\mathcal{N}_N, \\ \rho^0(\mathbf{r}) = \sum_{i\geq 1}n_i|\phi_i(\mathbf{r})|^2, \\ H^{\mathrm{EKS}}_{\rho_0}\phi_i = \epsilon_i\phi_i, \\ n_i = 1 \quad \text{if} \quad \epsilon_i < \epsilon_{\mathrm{F}}^0, \\ n_i = 0 \quad \text{if} \quad \epsilon_i > \epsilon_{\mathrm{F}}^0, \\ 0\leq n_i\leq 1 \quad \text{if} \quad \epsilon_i = \epsilon_{\mathrm{F}}^0, \\ H^{\mathrm{EKS}}_{\rho_0} = -\frac{1}{2}\Delta + V_{\mathrm{ne}} + \rho^0\star|\cdot|^{-1} + v^{\mathrm{xc}}(\rho^0), \end{cases}$$

where the Fermi level ϵ_{F}^0 is the Lagrange multiplier associated with the constrained $\sum_{i=1}^{\infty}n_i = N$. The difficulty of studying these models arises from the nonlinearity, non-convexity, and possible loss of compactness at infinity when $E_{\mathrm{xc}}\neq 0$ [1, 81].

Approximations of the exchange correlation energy

There are a large number of approximations of the exchange-correlation energy in the literature. Some of them, for instance the B3LYP functional [8] or the PBE functional [63] are very successful in many cases. However, despite recent progress [75], there are still problems for certain situations, for instance when Van-der-Waals (VDW) interaction plays a major role. Approximate exchange-correlation functionals can be classified in several groups:

- when E_{xc} is chosen identically equal to zero, we obtain the reduced Hartree-Fock model (rHF), also called the Hartee model;
- the simplest approximation actually used in practice is the local density approximation (LDA) [51, 65]:
$$E_{\text{xc}}^{\text{LDA}}(\rho) = \int_{\mathbb{R}^3} g(\rho(\mathbf{r}))\, d\mathbf{r},$$
where $g : \mathbb{R}_+ \to \mathbb{R}_-$ is the exchange-correlation energy density of the homogeneous electron gas. An approximation of the LDA model is the so-called Xα model [79]:
$$E_{\text{xc}}^{\text{X}\alpha}(\rho) = -C_D \int_{\mathbb{R}^3} \rho^{4/3},$$
where C_D is the Dirac constant;
- the generalized gradient approximation [63]. gives raise to exchange-correlation functionals of the form
$$E_{\text{xc}}^{\text{GGA}}(\rho) = \int_{\mathbb{R}^3} h(\rho, \frac{1}{2}|\nabla\sqrt{\rho}|^2),$$
where $h : \mathbb{R}_+ \times \mathbb{R}_+ \to \mathbb{R}_-$. The PBE functional previously mentioned belong to this class.

Let us mention more sophisticated approximations, such as meta-GGA [83] (e.g TPSS), hybrid functionals [8] (B3LYP, PBE0, HSE,...), range-separated functional [85], exact exchange (Ex), the random phase approximation for correlation [11, 12, 13] (cRPA), and functionals originated from the adiabatic connection fluctuation-dissipation theorem [60] (ACFD). As the complexity of the exchange-correlation energy functional increases, computational efficiency decreases [64]. This is represented usually by Jacob's ladder in DFT, which was first formulated by Perdew. It depicts five generations of exchange-correlation energy functionals leading from Hartree (the less accurate model) to the N-body Schr$\acute{}$odinger equation (the most accurate model), see figure (1.2).

A proof of existence of a Kohn-Sham ground state for neutral or positively charged systems was given in [81] for Hartree and in [1] for LDA. This question remains open for GGA and more complicated functionals.

1.2 Perturbation theory

Perturbation theory has various applications in quantum chemistry. It is used for instance to compute the response of the system under consideration to different chemical or electromagnetic environments. From a mathematical point of view, it aims at investigating

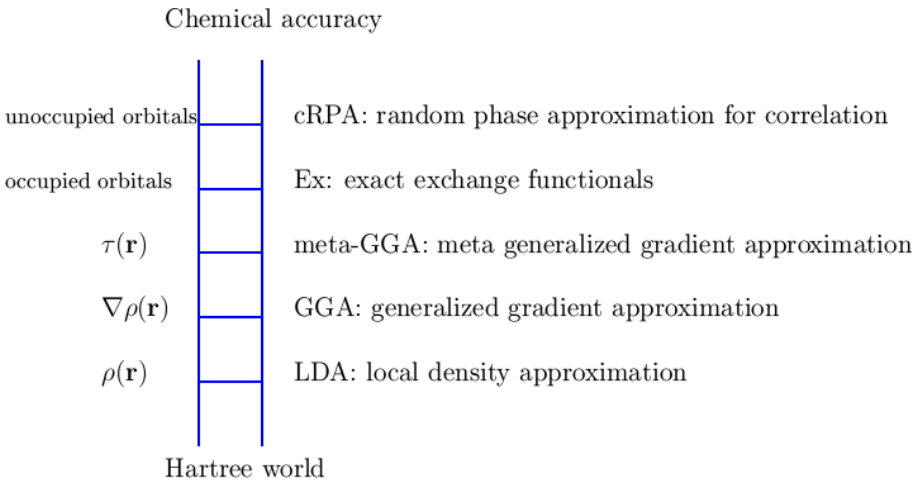

Figure 1.2 – Jacob's ladder of exchange-correlation energy functional [64].

how the eigenvalues and the eigenfunctions of a reference operator change when the later is slightly modified.

Eigenvalue perturbation theory was first introduced by Rayleigh [67] in the 1870's. The mathematical theory of the perturbation of linear operators has been first studied by Rellich [70]. We refer the reader to the reference books [47, 69].

The main results of perturbation theory will be recalled in this section. We will restrict ourselves to linear analytic perturbations in the sense of Kato [47]. A mathematical study of perturbation theory for some nonlinear quantum chemistry models, under some assumptions, can be found in the reference [21]. In chapter 2, we present a new approach to study the perturbation of such models, under more general assumptions. An important case for physical applications, which is not covered by analytic perturbation theory, namely the "stark effect", will be dealt with in chapters 3 and 4.

1.2.1 Finite dimensional perturbation

In this section, we present perturbation theory for the eigenvalue problem in a finite dimensional complex vector space X. We first focus on this case not only for simplicity, but also because the perturbation theory of discrete eigenvalues in infinite dimension can be reduced to the finite dimensional case.

For $z_0 \in \mathbb{C}$ and $R > 0$ we denote by $D(z_0, R) = \{z \in \mathbb{C} |\ |z - z_0| < R\}$ the disc in the complex plane of center z_0 and radius R and by $C(z_0, R) = \{z \in \mathbb{C} |\ |z - z_0| = R\}$ the circle in the complex plane of center z_0 and radius R.

Let $\beta \mapsto T(\beta) \in \mathcal{L}(X)$ be an operator-valued function of a complex variable β. Suppose that $T(\beta)$ is analytic in a given domain Ω of the complex plane. Without loss of generality, we can assume that $0 \in \Omega$. We have

$$T(\beta) = \sum_{\beta=0}^{\infty} \beta^k T^{(k)}.$$

with $T^{(k)} \in \mathcal{L}(X)$, the series being convergent for $|\beta|$ small. The operators $T = T^{(0)} = T(0)$ is the *unperturbed operator* and $A(\beta) = T(\beta) - T(0)$ is the *perturbation*. The eigenvalues of $T(\beta)$ satisfy the following characteristic equation

$$\det(E - T(\beta)) = 0. \tag{1.22}$$

Let $N = \dim(X)$. Equation (1.22) is a polynomial in E of degree N, with analytic coefficients in β. Thus, solving equation (1.22) for a given β is equivalent to finding the roots of

$$q(\beta, E) := \det(E - T(\beta)) = E^N + a_1(\beta)E^{N-1} + \cdots + a_N(\beta).$$

The functions $a_1(\beta) \cdots a_N(\beta)$ are analytic for $|\beta|$ small enough. Let E_0 be a root of $q(0, E)$ of multiplicity m. For $|\beta|$ small enough, it is known [50] that $q(\beta, E)$ has exactly m roots near E_0 and that these roots are the branches of one or more multivalued analytic functions. More precisely, there exist positive integers $p_1, \cdots, p_k$, with $\sum_{i=1}^{k} p_i = m$, such that the m roots of $q(\beta, E)$ near E_0 are given by multivalued functions $E_1(\beta), \cdots, E_k(\beta)$ analytic in $\beta^{\frac{1}{p_i}}$, for $i = 1, \cdots, k$, that is

$$E_i(\beta) = E_0 + \sum_{j=1}^{\infty} \alpha_j^{(i)} \beta^{\frac{j}{p_i}}. \tag{1.23}$$

These series are known as Puiseux series.

In particular, if E_0 is a simple root, then for $|\beta|$ small enough, there is exactly one root $E(\beta)$ of $q(\beta, E)$ near E_0. Moreover, $E(\beta)$ is analytic in β in the vicinity of 0.

For any operator A, we denote by $\sigma(A)$ the spectrum of A, and by $\rho(A) = \mathbb{C} \setminus \sigma(A)$ the resolvent set of A. The resolvent of $T(\beta)$ is defined by

$$\forall z \in \rho(T(\beta)), \quad R(\beta, z) := (z - T(\beta))^{-1}.$$

In fact, $R(\beta, z)$ is analytic in the two variables (β, z) in each domain in which z is not equal to an eigenvalue of $T(\beta)$ [47]. This result is obtained by writing $R(\beta, z)$ as follows

$$R(\beta, z) = R(0, z_0) \left[1 + (z - z_0 - A(\beta)) R(0, z_0)\right]^{-1},$$

where $z_0 \in \rho(T)$, and proving that the operator $(z - z_0 - A(\beta)) R(0, z_0)$ is small in norm for $|z - z_0|$ and $|\beta|$ small enough.

Let E be one of the eigenvalues of T, with multiplicity m, and $\epsilon > 0$ be such that $\sigma(T) \cap \overline{D(E, \epsilon)} = \{E\}$. Denote by, $\mathscr{C} = C(E, \epsilon)$ the circle in the complex plane of center E and radius ϵ. The analyticity of the resolvent $R(\beta, z)$, for $|\beta|$ small, insures the analyticity of the projector

$$\gamma(\beta) = -\frac{1}{2i\pi} \oint_{\mathscr{C}} R(\beta, z)\, dz.$$

In particular, if E_0 is a simple root of T with associated eigenvector ψ_0, then for $|\eta|$ small enough there exit analytic functions $\beta \mapsto E(\beta)$ and $\beta \mapsto \psi(\beta)$ from $D(0, \eta)$ into $\mathbb{C}$ and X respectively, satisfying $T(\beta)\psi(\beta) = E(\beta)\psi(\beta)$.

Additional results can be established when $T(\beta)$ is self-adjoint for β real. In this case, if $E^{(0)}$ is an eigenvalue of T of multiplicity m, then there exist $k \leq m$ distinct analytic functions in β near 0: $E_1(\beta), \cdots, E_k(\beta)$, which are all the eigenvalues of $T(\beta)$. This is known as Rellich's theorem [69]. In this particular case, one can show that in formula (1.23) for a given i, for any j, either $\alpha_j^{(i)} = 0$ or $\frac{j}{p_i}$ is an integer. Moreover, the associated eigenfunctions $\{\psi_i(\beta)\}_{1 \leq i \leq m}$ can be chosen orthonormalized and $\gamma(\beta)$ is then the orthogonal projector on the subspace spanned by those eigenfunctions.

Here are some elementary examples of linear perturbation in dimension two. For simplicity, $T(\beta)$ is identified by its matrix representation.

1. First example:
$$T(\beta) = \begin{pmatrix} 1 & \beta \\ \beta & -1 \end{pmatrix}.$$
This is an example where the eigenvalues form the branches of one double-valued function, with two exceptional points, where there is "level crossing" between the two eigenvalues. The eigenvalues of $T(\beta)$ are: $E_\pm = \pm(1+\beta^2)^{\frac{1}{2}}$, and $\beta = \pm i$ are the exceptional points. The eigenprojectors are:
$$P_\pm(\beta) = \pm \frac{1}{2(1+\beta^2)^{\frac{1}{2}}} \begin{pmatrix} 1 \pm (1+\beta^2)^{\frac{1}{2}} & \beta \\ \beta & -1 \pm (1+\beta^2)^{\frac{1}{2}} \end{pmatrix}.$$

2. Second example:
$$T(\beta) = \begin{pmatrix} 0 & \beta \\ \beta & 0 \end{pmatrix}.$$
This is an example where the eigenvalues are two distinct analytic functions, with an exceptional point. The eigenvalues of $T(\beta)$ are: $E_\pm = \pm\beta$, and $\beta = 0$ is an exceptional point. The eigenprojectors are:
$$P_1(\beta) = \frac{1}{2} \begin{pmatrix} 1 & 1 \\ 1 & 1 \end{pmatrix}, \quad P_2(\beta) = \frac{1}{2} \begin{pmatrix} 1 & -1 \\ -1 & 1 \end{pmatrix}.$$

3. Third example:
$$T(\beta) = \begin{pmatrix} 0 & \beta \\ 0 & 0 \end{pmatrix}.$$
This is an example where we have two identical analytic functions, with no exceptional points. For all $\beta \in \mathbb{C}$, 0 is an eigenvalue of $T(\beta)$ of multiplicity two. The eigenprojector is the identity.

4. Fourth example:
$$T(\beta) = \begin{pmatrix} 0 & 1 \\ \beta & 0 \end{pmatrix}.$$
This is an example where the eigenvalues are the branches of one double-valued function, with one exceptional point. The eigenvalues of $T(\beta)$ are: $E_\pm = \pm\beta^{\frac{1}{2}}$, and $\beta = 0$ is an exceptional point. The eigenprojectors are:
$$P_\pm(\beta) = \frac{1}{2} \begin{pmatrix} 1 & \pm\beta^{-\frac{1}{2}} \\ \pm\beta^{-\frac{1}{2}} & 1 \end{pmatrix}.$$

5. Fifth example:

$$T(\beta) = \begin{pmatrix} 1 & \beta \\ 0 & 0 \end{pmatrix}.$$

This is an example where the eigenvalues are two distinct analytic functions, with no exceptional point. The eigenvalues of $T(\beta)$ are: 0 and 1. The eigenprojectors are:

$$P_1(\beta) = \begin{pmatrix} 1 & \beta \\ 0 & 0 \end{pmatrix}, \quad P_2(\beta) = \begin{pmatrix} 0 & -\beta \\ 0 & 1 \end{pmatrix}.$$

6. Sixth example:

$$T(\beta) = \begin{pmatrix} \beta & 1 \\ 0 & 0 \end{pmatrix}.$$

This is an example where the eigenvalues are two distinct analytic functions, with one exceptional point. The eigenvalues of $T(\beta)$ are: 0 and β, and $\beta = 0$ is the exceptional point. The eigenprojectors are:

$$P_1(\beta) = \begin{pmatrix} 1 & \beta^{-1} \\ 0 & 0 \end{pmatrix}, \quad P_2(\beta) = \begin{pmatrix} 0 & -\beta^{-1} \\ 0 & 1 \end{pmatrix}.$$

1.2.2 Regular perturbation theory

In the previous section, we introduced perturbation theory in finite dimensional complex vector spaces. In this section, we will extend the results to an infinite-dimensional complex Hilbert space X.

Let $T(\beta)$ be an operator-valued function on a domain Ω of the complex plane, such that for every $\beta \in \Omega$, the operator $T(\beta)$ is closed and the resolvent set $\rho(T(\beta))$ is non-empty. We define the following two types of analytic operators:

- we say that the operator $T(\beta)$ is analytic in the sense of Kato, if and only if, for every $\beta_0 \in \Omega$, there exists $z_0 \in \rho(T(\beta_0))$ and $\eta > 0$ such that $z_0 \in \rho(T(\beta))$ for all $\beta \in D(\beta_0, \eta)$ and $D(\beta_0, \eta) \ni \beta \mapsto (z_0 - T(\beta))^{-1}$ is analytic.
- we say that $T(\beta)$ is an analytic family of type **(A)** if and only if
  - the operator domain of $T(\beta)$ is some dense subspace $D \subset X$ independent of β;
  - for each $\psi \in D$, $T(\beta)\psi$ is a vector-valued analytic function of β. That is

$$T(\beta)\psi = T\psi + \beta T^{(1)}\psi + \beta^2 T^{(2)}\psi + \cdots,$$

which is convergent in a disc independent of ψ.

It is to be remarked that an analytic family of type **(A)** is analytic in the sense of Kato.

We assume here that $\beta \mapsto T(\beta)$ is self-adjoint for β real and analytic in the sense of Kato. It is straightforward to show that the results obtained in finite dimension can be extended to isolated eigenvalues of $T(0)$, without substantial modifications. This can be achieved by restricting the operator $T(\beta)$ to the subspace spanned by the eigenfunctions

associated to the discrete eigenvalue under consideration and using the results obtained for the finite-dimensional problem.

Without loss of generality, we can suppose that $0 \in \Omega$ and $\beta_0 = 0$. Let $E^{(0)}$ be an eigenvalue of T of multiplicity m. Then there exist $\epsilon > 0$ and $\eta > 0$ such that for all $\beta \in D(0,\eta)$, $T(\beta)$ has exactly m eigenvalues $E_1(\beta), \cdots, E_m(\beta)$ in $D(E^{(0)}, \epsilon)$. The functions $\beta \mapsto E_1(\beta), \cdots, \beta \mapsto E_m(\beta)$ are simple valued analytic functions in $D(0,\eta)$, with $E_k(0) = E^{(0)}$.

The set

$$\Gamma := \{(\beta, z); \quad \beta \in \Omega, \quad z \in \rho(T(\beta))\}$$

is open, and the resolvent function

$$R(\beta, z) := (z - T(\beta))^{-1}$$

defined on Γ is analytic in the two variables (β, z) [69]. Let $\mathscr{C} = C(E^{(0)}, \epsilon)$ be a circle in the complex plane of center $E^{(0)}$ and radius $\epsilon > 0$ such that $\sigma(T) \cap \overline{D(E^{(0)}, \epsilon)} = \{E^{(0)}\}$. Since $\mathscr{C}$ is compact and Γ is open, there exists $\eta > 0$, such that $z \notin \sigma(T(\beta))$ if $|z - E^{(0)}| = \epsilon$ and $|\beta| \leq \eta$. Therefore the projector

$$\gamma(\beta) := \frac{1}{2i\pi} \oint_{\mathscr{C}} R(\beta, z)\, dz \tag{1.24}$$

is well-defined and is analytic for $|\beta| \leq \delta$. The analyticity of the above projector follows from the analyticity of the resolvent $R(\beta, z)$. In fact, when β is real, the projector defined in (1.24) is the orthogonal projector over the vector subspace of dimension m generated by the eigenvectors of $T(\beta)$ associated to the eigenvalues $E_1(\beta), \cdots, E_m(\beta)$.

In particular, we get the Kato-Rellich theorem [69]: if E_0 is a simple eigenvalue of T with associated eigenvector ψ_0, then there exists one point $E(\beta) \in \sigma(T(\beta)) \cap \overline{D(E_0, \epsilon)}$, such that $E(\beta)$ is a simple eigenvalue of $T(\beta)$, which is analytic for $|\beta|$ small. Furthermore, there exists an analytic associated eigenvector $\psi(\beta)$:

$$T(\beta)\psi(\beta) = E(\beta)\psi(\beta).$$

when β is real, one can take $\psi(\beta) = \mathbb{1}_I(T(\beta))\psi_0$, where $I =]E_0 - \epsilon, E_0 + \epsilon[$ or the normalized eigenvector

$$\psi(\beta) = \langle \psi_0, \mathbb{1}_I(T(\beta))\psi_0 \rangle^{-\frac{1}{2}} \mathbb{1}_I(T(\beta))\psi_0.$$

Note that, $\langle \psi_0, \mathbb{1}_I(T(\beta))\psi_0 \rangle \neq 0$ for $|\beta|$ small, since $\mathbb{1}_I(T(\beta))\psi_0 \to \psi_0$ as $\beta \to 0$.

1.2.3 Linear Perturbation theory

We now consider a special family of analytic operators, which is often encountered in quantum chemistry,namely the following linearly perturbed operator

$$H(\beta) = H_0 + \beta V, \tag{1.25}$$

where H_0 is a self-adjoint operator on $\mathcal{H}$ with domain $D(H_0)$, $\mathcal{H}$ being a real Hilbert space, and where V is the perturbation operator. The number β is called the coupling constant in quantum mechanics. The operator $H(\beta)$, defined on $D(H_0) \cap D(V)$, is an analytic family of type **(A)**, for β near 0, if and only if V is H_0-bounded, that is

- $D(H_0) \subset D(V)$,
- there exist $a, b > 0$ such that $\|V\psi\|_{\mathcal{H}} \leq a\|H_0\psi\|_{\mathcal{H}} + b\|\psi\|_{\mathcal{H}}$, for any $\psi \in D(H_0)$.

For example, let $V \in L^2(\mathbb{R}^d) + L^\infty(\mathbb{R}^d)$ and $H_0 = -\Delta$ on $\mathbb{R}^d$, then $H_0 + \beta V$ is a family of type **(A)** on $\mathcal{H} = L^2(\mathbb{R}^d)$ with $D = H^2(\mathbb{R}^d)$.

Moreover, if the function V is infinitesimally small with respect to H_0 (that is if a can be chosen as small as we wish), then $H_0 + \beta V$ is an entire family of type **(A)**, that is analytic on $\mathbb{C}$.

Note that an operator $H_0 + \beta V$, where V is symmetric and H_0-bounded, is self-adjoint for $|\beta|$ small enough. This result is known as the Kato-Rellich theorem [61, p 145-167].

Let $H_0 + \beta V$ be an analytic family in the sense of Kato. Let $E_0 \in \sigma_d(H_0)$ be a simple eigenvalue of H_0. The results stated above are valid for this type of operators, that is the existence, uniqueness and analyticity of the eigenvalues of $H_0 + \beta V$, in a neighborhood of E_0, and of their associated eigenprojector is guaranteed for $|\beta|$ small. In the following, we will recall well-known formulas for the computation of the coefficients in the Taylor expansions. We distinguish two cases:

- case 1: $E^{(0)}$ is a simple eigenvalue of H_0 with associated eigenvector $\psi^{(0)} \in D(H_0)$. The simple perturbed eigenvalue in $I =]E_0 - \epsilon, E_0 + \epsilon[$ of the linearly perturbed operator $H(\beta) = H_0 + \beta V$ and its associated eigenvector exist and are analytic for $|\beta|$ small enough. Their Taylor series are, respectively,

$$E(\beta) = \sum_{n\in\mathbb{N}} \beta^n E^{(n)} \quad \text{and} \quad \psi(\beta) = \sum_{n\in\mathbb{N}} \beta^n \psi^{(n)}. \tag{1.26}$$

  These series are called Rayleigh-Schrödinger series. They are normally convergent in $\mathbb{R}$ and $D(H_0)$, respectively. For $|\beta|$ small, the Rayleigh-Schrödinger coefficients of (1.26) are determined by the well-posed triangular system

$$\forall n \in \mathbb{N}^* \quad \begin{cases} \left(H_0 - E^{(0)}\right) = f_n + E^{(n)}\psi^{(n)} \\ \langle\psi^{(0)}|\psi^{(n)}\rangle = \alpha_n, \end{cases}$$

  where $f_n = -V\psi^{(n-1)} + \sum_{k=1}^{n-1} E^{(k)}\psi^{(n-k)}$ and $\alpha_n = -\frac{1}{2}\sum_{k=1}^{n-1}\langle\psi^{(k)}|\psi^{(n-k)}\rangle$. In particular,

$$E^{(1)} = \langle\psi^{(0)}|V|\psi^{(0)}\rangle.$$

  If H_0 is diagonalizable in an orthonormal basis, that is if

$$H_0 = \sum_{k\in\mathbb{N}} \epsilon_k |\phi_k\rangle\langle\phi_k|,$$

  with $\langle\phi_l|\phi_k\rangle = \delta_{lk}$ and $(\epsilon_0, \phi_0) = (E^{(0)}, \psi^{(0)})$, we have the *sum-over-state formula*

$$\psi^{(1)} = -\sum_{k\in\mathbb{N}^*} \frac{\langle\phi_k|V|\phi_0\rangle}{\epsilon_k - \epsilon_0}, \quad E^{(2)} = -\sum_{k\in\mathbb{N}^*} \frac{|\langle\phi_k|V|\phi_0\rangle|^2}{\epsilon_k - \epsilon_0} \quad ...$$

  In numerical simulations, it is preferred to solve the triangular system (1.27) rather than using the sum-over-state formula, as the later requires the knowledge of all the eigenstates of H_0;

- case 2: $E^{(0)}$ is a multiple eigenvalue of H_0. Denote by $P_0 = \gamma(0) = \mathbb{1}_I(H_0)$. The eigenprojector of the linearly perturbed operator $H(\beta) = H_0 + \beta V$ defined by (1.24) is analytic in β, for $|\beta|$ small. This projector can be written as a convergent series, called the Dyson expansion, as follows

$$\mathbb{1}_I(H_0 + \beta V) = \sum_{n=0}^{N} \beta^n P_n + \beta^{N+1} R_N = \sum_{n=0}^{\infty} \beta^n P_n,$$

with

$$P_n = \tfrac{1}{2i\pi} \oint_{\mathscr{C}} \left[(z - H_0)^{-1} V\right]^n (z - H_0)^{-1}\, dz,$$

$$R_N = \tfrac{1}{2i\pi} \oint_{\mathscr{C}} \left[(z - H_0)^{-1} V\right]^{N+1} (z - (H_0 + \beta V))^{-1}\, dz,$$

where $\mathscr{C}$ is a circle in the complex domain of center $E^{(0)}$ and small radius. This Dyson series is normally convergent in the space $\mathcal{L}(\mathcal{H})$ of bounded operators on $\mathcal{H}$. It is also convergent in stronger topologies such as $\mathfrak{S}_1(\mathcal{H}) = \{\gamma \in \mathcal{L}(\mathcal{H});\, \mathrm{Tr}\,(|\gamma|) < \infty\}$.

One can find an explicit lower bound on the radius of convergence of the above stated series [47]. For simplicity, suppose that V is H_0-bounded, and that $E^{(0)}$ is a simple eigenvalue of H_0. We have, $\|V\psi\|_{\mathcal{H}} \leq a\|H_0\psi\|_{\mathcal{H}} + b\|\psi\|_{\mathcal{H}}$, for any $\psi \in D(H_0)$. Let $d = \frac{1}{2}\mathrm{dist}\left(E^{(0)}, \sigma(H_0) \setminus \{E^{(0)}\}\right)$. Then the eigenvalue $E(\beta)$ of $H_0 + \beta V$ near $E^{(0)}$ is analytic in the disc of radius r_0, given by

$$r_0 = \left[a + d^{-1}\left[b + a(|E^{(0)}| + d)\right]\right]^{-1}.$$

Finally, we will illustrate with the following example that the analytic continuation of an eigenvalue is not necessarily an eigenvalue. This is in contrast to the finite dimensional case, where the analytic continuation of an eigenvalue always remains an eigenvalue. Let $H_0 = -\Delta - \frac{1}{|r|}$ and $V = \frac{1}{|r|}$. Then the eigenvalues of $H_0 + \beta V$ are $-\frac{1}{4n^2}(1 - \beta)^2$, for $n = 1, 2, \cdots$, and $|\beta|$ small. The ground state energy is $E^{(0)}(\beta) = -\frac{1}{4} + \frac{1}{2}\beta + \frac{1}{4}\beta^2$. Even though $E^{(0)}$ is given by an entire function, $H_0 + \beta V$ has no eigenvalues at all for $\beta > 1$.

1.3 Main results

In this section, we summarize the results obtained during this PhD work, which are detailed in the coming three chapters.

1.3.1 Density functional perturbation theory

Consider a neutral or positively charged molecular system, containing N electrons subjected to a nuclear potential V. We define the following energy functional

$$E^{\mathrm{rHF}}(\gamma, W) := \mathrm{Tr}\left(-\frac{1}{2}\Delta\gamma\right) + \int_{\mathbb{R}^3} \rho_\gamma V + \frac{1}{2}D(\rho_\gamma, \rho_\gamma) + \int_{\mathbb{R}^3} \rho_\gamma W,$$

and the minimization problem

$$\mathcal{E}^{\mathrm{rHF}}(W) := \inf\left\{E^{\mathrm{rHF}}(\gamma, W),\ \gamma \in \mathcal{K}_N\right\}, \tag{1.27}$$

where $\mathcal{K}_N$ is defined in (1.19). The potential W is the perturbation potential and it belongs to the space $\mathcal{C}'$, the dual of the Coulomb space $\mathcal{C}$ (see Section 2.2) for precise definition of these spaces.

Unperturbed system

When the perturbation is turned off, i.e. $W = 0$, it is known that problem (1.27) has a minimizer γ_0 and that all the ground states share the same density ρ_0. The mean-field-Hamiltonian

$$H_0 := -\frac{1}{2}\Delta + V + \rho_0 \star |\cdot|^{-1},$$

is a self-adjoint operator on $L^2(\mathbb{R}^3)$ and any ground state γ_0 is of the form

$$\gamma_0 = \mathbb{1}_{(-\infty,\epsilon_{\rm F}^0)}(H_0) + \delta_0,$$

with $\epsilon_{\rm F}^0 \leq 0$, $0 \leq \delta_0 \leq 1$, $\mathrm{Ran}(\delta_0) \subset \mathrm{Ker}(H_0 - \epsilon_{\rm F}^0)$ [81]. The number $\epsilon_{\rm F}^0 \leq 0$ is the Fermi level. We distinguish the following three cases

- **case 1 (non-degenerate case):** H_0 has at least N negative eigenvalues and $\epsilon_N < \epsilon_{N+1} \leq 0$,
- **case 2 (degenerate case):** H_0 has at least $N+1$ negative eigenvalues and $\epsilon_{N+1} = \epsilon_N$,
- **case 3 (singular case):** $\epsilon_{\rm F}^0 = \epsilon_N = 0$,

where ϵ_i is the i's non-positive eigenvalue of H_0. We denote by (ϕ_i^0) an orthonormal family of associated eigenvectors. In the non-degenerate case, the ground state is unique: it is the orthogonal projector $\gamma_0 = \mathbb{1}_{(-\infty,\epsilon_{\rm F}^0)}(H_0) = \sum_{i=1}^N |\phi_i^0\rangle\langle\phi_i^0|$. In the degenerate case, we introduce the following assumption: for any real symmetric matrix M of dimension $N_{\rm p}$, we have

$$\left(\forall x \in \mathbb{R}^3,\ \sum_{i,j=1}^{N_{\rm p}} M_{ij}\phi_{N_{\rm f}+i}^0(x)\phi_{N_{\rm f}+j}^0(x) = 0 \right) \ \Rightarrow\ M = 0,$$

where $N_{\rm f} := \mathrm{Rank}\left(\mathbb{1}_{(-\infty,\epsilon_{\rm F}^0)}(H_0)\right)$ is the number of (fully occupied) eigenvalues lower than $\epsilon_{\rm F}^0$, and $N_{\rm p} := \mathrm{Rank}\left(\mathbb{1}_{\{\epsilon_{\rm F}^0\}}(H_0)\right)$ is the number of (partially occupied) bound states of H_0 with energy $\epsilon_{\rm F}^0$. This assumption guarantees the uniqueness of the ground state γ_0 in the degenerate case. In Section (2.2), we identify two situations where this assumption is valid.

Perturbed system

Let us now turn on the perturbation, that is we consider the case when $W \neq 0$. For the non-degenerate case, we prove that there exists $\eta > 0$, such that for all $W \in B_\eta(\mathcal{C}')$, (1.27) has a unique minimizer γ_W. In addition, γ_W is an orthogonal projector of rank N and

$$\gamma_W = \mathbb{1}_{(-\infty,\epsilon_{\rm F}^0)}(H_W) = \frac{1}{2i\pi}\oint_{\mathscr{C}} (z - H_W)^{-1}\, dz,$$

where

$$H_W = -\frac{1}{2}\Delta + V + \rho_W \star |\cdot|^{-1} + W,$$

ρ_W being the density of γ_W. Moreover, the mappings $W \mapsto \gamma_W$, $W \mapsto \rho_W$ and $W \mapsto \mathcal{E}^{\mathrm{rHF}}(W)$ are real analytic from $B_\eta(\mathcal{C}')$ into $\mathfrak{S}_{1,1}$, $\mathcal{C}$ and $\mathbb{R}$ respectively, where $B_\eta(\mathcal{C}')$ denotes the ball of $\mathcal{C}'$ with center 0 and radius η and $\mathfrak{S}_{1,1} := \{T \in \mathfrak{S}_1 \mid |\nabla|T|\nabla| \in \mathfrak{S}_1\}$ where $\mathfrak{S}_1$ is the space of trace class operators. Therefore, for all $W \in \mathcal{C}'$ and all $-\eta\|W\|_{\mathcal{C}'}^{-1} < \beta < \eta\|W\|_{\mathcal{C}'}^{-1}$,

$$\gamma_{\beta W} = \gamma_0 + \sum_{k=1}^{+\infty} \beta^k \gamma_W^{(k)}, \quad \rho_{\beta W} = \rho_0 + \sum_{k=1}^{+\infty} \beta^k \rho_W^{(k)},$$

and

$$\mathcal{E}^{\mathrm{rHF}}(\beta W) = \mathcal{E}(0) + \sum_{k=1}^{+\infty} \beta^k \mathcal{E}_W^{(k)},$$

the series being normally convergent in $\mathfrak{S}_{1,1}$, $\mathcal{C}$ and $\mathbb{R}$ respectively. A recursion relation is given to compute the Rayleigh-Schrödinger coefficients $\gamma_W^{(k)}, \rho_W^{(k)}$ and $\mathcal{E}_W^{(k)}$. Finally, Wigner's $(2n+1)$-rule, which states that the knowledge of $\gamma_W^{(k)}$ for $k \leq n$ is enough to compute $\gamma_W^{(2n)}$ and $\gamma_W^{(2n+1)}$, is rigorously proved. Some of these results were already known in the literature (for instance see [21]).

Our main original results are concerned with the degenerate case. We assume that the natural occupation numbers at the Fermi level are strictly comprised between 0 and 1. As a consequence, γ_0 belongs to the subset

$$\mathcal{K}_{N_\mathrm{f},N_\mathrm{p}} := \{\gamma \in \mathcal{K}_N \mid \mathrm{Rank}(\gamma) = N_\mathrm{f} + N_\mathrm{p},\ \dim(\mathrm{Ker}(1-\gamma)) = N_\mathrm{f}\}$$

of $\mathcal{K}_N$. In order to establish similar results as in the non-degenerate case, we proceed as follows

1. we first construct a real analytic local chart of $\mathcal{K}_{N_\mathrm{f},N_\mathrm{p}}$ in the vicinity of γ_0;
2. we use this local chart to prove that, for $\|W\|_{\mathcal{C}'}$ small enough, the minimization problem
$$\widetilde{\mathcal{E}}^{\mathrm{rHF}}(W) := \inf\left\{E^{\mathrm{rHF}}(\gamma, W),\ \gamma \in \mathcal{K}_{N_\mathrm{f},N_\mathrm{p}}\right\}$$
has a unique local minimizer γ_W in the vicinity of γ_0, and that the mappings $W \mapsto \gamma_W \in \mathfrak{S}_{1,1}$ and $W \mapsto \widetilde{\mathcal{E}}^{\mathrm{rHF}}(W)$ are real analytic; we then prove that γ_W is actually the unique global minimizer of (2.4), hence that $\widetilde{\mathcal{E}}^{\mathrm{rHF}}(W) = \mathcal{E}^{\mathrm{rHF}}(W)$;
3. we finally derive the coefficients of the Rayleigh-Schrödinger expansions of γ_W and $\mathcal{E}^{\mathrm{rHF}}(W)$, and prove that Wigner's $(2n+1)$-rule also holds true in the degenerate case.

Finally, we comment on the ability of extending our approach to other settings, such as Kohn-Sham LDA model (under some additional assumptions).

1.3.2 Pseudopotentials

Pseudopotential methods are widely used in electronic structure calculations. These methods rely on the fact that the core electrons of an atom are hardly affected by the chemical environment experienced by this atom. In pseudopotential methods, core electrons are

frozen in a state computed once and for all from an atomic calculation, while valence electrons are described by pseudo-orbitals. As a pseudopotential is constructed from atomic calculation only, we just consider atomic models in this section. We restrict ourselves to the Hartree model. Extensions to the Kohn-Sham LDA model are discussed in Chapter 3.

On one hand, we have the ground state all-electron density matrix γ_z^0 of the atom with nuclear charge z (which we abbreviate as atom z in the sequel), which is a solution to

$$I_z^{\mathrm{AA}} := \inf\left\{E_z^{\mathrm{AA}}(\gamma),\ \gamma \in \mathcal{K}_z\right\},$$

where

$$E_z^{\mathrm{AA}}(\gamma) = \mathrm{Tr}\left(-\frac{1}{2}\Delta\gamma\right) - z\int_{\mathbb{R}^3}\frac{\rho_\gamma(\mathbf{r})}{|\mathbf{r}|}\,d\mathbf{r} + \frac{1}{2}D\left(\rho_\gamma,\rho_\gamma\right).$$

The ground state all-electron density (which is unique by a strict convexity argument) is defined by $\rho_z^0 := \rho_{\gamma_z^0}$. The Hartree all-electron atomic Hamiltonian

$$H_z^{\mathrm{AA}} = -\frac{1}{2}\Delta + W_z^{\mathrm{AA}}, \quad \text{where} \quad W_z^{\mathrm{AA}} = -\frac{z}{|\cdot|} + \rho_z^0 \star |\cdot|^{-1},$$

is a bounded below self-adjoint operator on $L^2(\mathbb{R}^3)$ with domain $H^2(\mathbb{R}^3)$. Due to symmetries, W_z^{AA} is radial so that finding the eigenfunctions of H_z^{AA} reduces to solving the family of radial Schrödinger equations (index by the quantum number $l \in \mathbb{N}$, see Chapter 3 for details),

$$\begin{cases} R_{z,n,l} \in H^1(\mathbb{R}), \quad R_{z,n,l}(-r) = R_{z,n,l}(r) \text{ for all } r \in \mathbb{R}, \\ -\frac{1}{2}R''_{z,n,l}(r) + \frac{l(l+1)}{2r^2}R_{z,n,l}(r) + W_z^{\mathrm{AA}}(r)R_{z,n,l}(r) = \epsilon_{z,n,l}R_{z,n,l}(r), \\ \int_{\mathbb{R}} R_{z,n,l}^2 = 1, \end{cases}$$

where $\epsilon_{z,n,l}$ are the eigenvalues of H_z^{AA}, ordered in such a way that $\epsilon_{z,1,l} \leq \epsilon_{z,2,l} \leq \cdots$ for all l. For each $l \leq l_z$ (l_z is a well-chosen non-negative integer), we denote by $n_{z,l}^\star$, the unique non-negative integer such that $\epsilon_{z,n_{z,l}^\star,l}$ correspond to a valence electron. The choice of l_z and the existence of $n_{z,l}^\star$ are discussed in Chapter 3.

On the other hand, the ground state pseudo-density matrix $\widetilde{\gamma}_z^0$ of atom z is the solution of

$$I_z^{\mathrm{PP}} = \inf\left\{E_z^{\mathrm{PP}}(\widetilde{\gamma}),\ \widetilde{\gamma} \in \mathcal{K}_{N_{z,\mathrm{v}}}\right\},$$

where

$$E_z^{\mathrm{PP}}(\widetilde{\gamma}) = \mathrm{Tr}\left(\left(-\frac{1}{2}\Delta + V_z^{\mathrm{PP}}\right)\widetilde{\gamma}\right) + \frac{1}{2}D\left(\rho_{\widetilde{\gamma}},\rho_{\widetilde{\gamma}}\right),$$

$N_{z,\mathrm{v}}$ is the number of valence electrons and V_z^{PP} is the pseudopotential, which is a non-local rotation-invariant operator. The pseudo-density is defined by $\widetilde{\rho}_z^0 := \rho_{\widetilde{\gamma}_z^0}$ is unique and radial. The Hartree pseudo-Hamiltonian

$$H_z^{\mathrm{PP}} = -\frac{1}{2}\Delta + W_z^{\mathrm{PP}}, \quad \text{where} \quad W_z^{\mathrm{PP}} = V_z^{\mathrm{PP}} + \widetilde{\rho}_z^0 \star |\cdot|^{-1},$$

corresponding to the pseudopotential $V_z^{\rm PP}$, is a bounded below self-adjoint operator on $L^2(\mathbb{R}^3)$ with domain $H^2(\mathbb{R}^3)$. Due to symmetries, its eigenvalues are obtained by solving the family of Schrödinger equations

$$\left\{\begin{array}{l} \widetilde{R}_{z,n,l} \in H^1(\mathbb{R}), \quad \widetilde{R}_{z,n,l}(-r) = \widetilde{R}_{z,n,l}(r) \text{ for all } r \in \mathbb{R}, \\ \\ -\frac{1}{2}\widetilde{R}''_{z,n,l}(r) + \frac{l(l+1)}{2r^2}\widetilde{R}_{z,n,l}(r) + W_{z,l}^{\rm PP}(r)\widetilde{R}_{z,n,l}(r) = \epsilon_{z,n,l}^{\rm PP}\widetilde{R}_{z,n,l}(r), \\ \\ \int_{\mathbb{R}} \widetilde{R}_{z,n,l}^2 = 1, \end{array}\right. \tag{1.28}$$

where $W_{z,l}^{\rm PP} = P_l W_z^{\rm PP} P_l$, P_l denoting the orthogonal projector from $L^2(\mathbb{R}^3)$ on the subspace $\mathrm{Ker}(\mathbf{L}^2 - l(l+1))$ ($\mathbf{L}$ is the angular momentum operator). For semilocal norm-conserving pseudopotentials, $W_{z,l}^{\rm PP}$ is a multiplication operator.

The norm-conserving pseudopotentials $V_z^{\rm PP}$ are constructed in such a way that

1. the occupied eigenfunctions of the pseudo-Hamiltonian agree with the valence all-electron eigenfunctions outside the core region, more precisely

$$\widetilde{R}_{z,1,l} = R_{z,n_{z,l}^\star,l} \quad \text{on} \quad (r_{\rm c}, +\infty),$$

   where $r_{\rm c}$ is the core radius, chosen larger than the largest node of $R_{z,n_{z,l}^\star,l}$, for all $l \leq l_z$;

2. the functions $\widetilde{R}_{z,1,l}$ have no nodes other than zero;

$$\int_{\mathbb{R}} \widetilde{R}_{z,1,l}^2 = 1 \quad \text{and} \quad R_{z,1,l} > 0 \quad \text{on} \quad (0,\infty);$$

3. the lowest eigenvalues of the pseudo-Hamiltonian are equal to the valence all-electron eigenvalues, more precisely

$$\epsilon_{z,n_{z,l}^\star,l} = \epsilon_{z,1,l}^{\rm PP}.$$

The advantage of the pseudopotential methods, besides the fact that they reduce the number of electrons explicitly dealt with, is that the pseudo-orbitals can be made more regular in the core region than the valence all-electron orbitals. The former can therefore be represented numerically in less expensive ways (with a lower number of basis functions or on coarser meshes). In addition, pseudopotentials can be used to incorporate relativistic effects in non-relativistic calculations.

In Chapter 3, we prove that, if the Fermi level $\epsilon_{z,\rm F}^0$ is negative and $r_{\rm c}$ is large enough, there exists a pseudopotential of arbitrary Sobolev regularity satisfying the above requirements. We also prove that, under the assumption that $\epsilon_{z,\rm F}^0$ is not an accidentally degenerate eigenvalue of $H_z^{\rm AA}$, the set of the admissible pseudopotentials of local regularity H^s ($s > 0$) is a weakly closed subset of an affine space endowed with an H^s norm.

Moreover, with more restricted conditions, for each $0 \leq l \leq l_z$, the radial function $\widetilde{R}_{z,1,l}$ is regular and

$$\widetilde{R}_{z,1,l}(r) = O(r^{l+1}) \quad \text{as} \quad r \to 0.$$

The above property is used in practice to build pseudo-orbitals from which the local and nonlocal components of the atomic pseudopotential are calculated by inversion of the radial Schrödinger equations (1.28) (see e.g. [87]).

Some stability results of the Hartree ground state with respect to both external perturbations and small variations of the pseudopotential are proved. Our analysis encompasses the case of Stark perturbation potentials generated by uniform electric fields.

Finally, we propose a new way to construct pseudopotentials, consisting in choosing the best candidate in the set of all admissible pseudopotentials for a given optimality criterion.

1.3.3 Numerical simulations

This section is devoted to stating the numerical results obtained for the discretization of the Kohn-Sham model for atoms in the reduced Hartree-Fock and Kohn-Sham LDA models [51, 65]. Both isolated atoms and atoms subjected to cylindrically symmetric external potentials are considered. For simplicity, we restrict ourselves to restricted spin-collinear Kohn-Sham models. Recall that, for a molecular system with one nucleus of charge z and N electrons subjected to an external potential βW ($\beta \in \mathbb{R}$ is the coupling constant), the energy functional to be minimized reads

$$\widetilde{E}_{z,N}^{\mathrm{rHF/LDA}}(\gamma, \beta W) := E_{z,N}^{\mathrm{rHF/LDA}}(\gamma) + \int_{\mathbb{R}^3} \beta W \rho_\gamma, \tag{1.29}$$

and is well-defined for any $\gamma \in \mathcal{K}_N$, $W \in \mathcal{C}'$ and $\beta \in \mathbb{R}$, for both the reduced Hartree-Fock model

$$E_{z,N}^{\mathrm{rHF}}(\gamma) := \mathrm{Tr}\left(-\frac{1}{2}\Delta\gamma\right) - z\int_{\mathbb{R}^3} \frac{\rho_\gamma}{|\cdot|} + \frac{1}{2}D(\rho_\gamma, \rho_\gamma),$$

and the Kohn-Sham LDA model

$$E_{z,N}^{\mathrm{LDA}}(\gamma) := \mathrm{Tr}\left(-\frac{1}{2}\Delta\gamma\right) - z\int_{\mathbb{R}^3} \frac{\rho_\gamma}{|\cdot|} + \frac{1}{2}D(\rho_\gamma, \rho_\gamma) + E_{\mathrm{xc}}^{\mathrm{LDA}}(\rho_\gamma),$$

(see Section 1.1.6). Denote by

$$\widetilde{\mathcal{I}}_{z,N}^{\mathrm{rHF/LDA}}(\beta W) := \inf\left\{\widetilde{E}_{z,N}^{\mathrm{rHF/LDA}}(\gamma, \beta W),\ \gamma \in \mathcal{K}_N\right\}. \tag{1.30}$$

In Chapter 4, a-finite dimensional submanifold $\mathcal{K}_{N,h}$ of $\mathcal{K}_N$ is constructed, and a variational approximation of (1.30) is obtained by minimizing the energy functional (1.29) over the approximation set $\mathcal{K}_{N,h}$. A practical reformulation of the discretized problem and of its Euler-Lagrange equations is presented. Solving these Euler-Lagrange equations amounts to solving a generalized nonlinear eigenvalue problem. The description of the self-consistent algorithm we use to solve this problem is also detailed. Our numerical results can be divided into two categories:

1. for isolated atoms ($W = 0$):

   - we study the ground state energy and the energy levels of the discretized problem as a function of the cut-off radius (we solve the Kohn-Sham equations in a large ball centered at the nucleus with Dirichlet boundary conditions) and the mesh size;

- we provide the occupied energy levels in the rHF and Xα cases for all the atoms of the first four rows of the periodic table ($1 \leq z \leq 54$). It is to be noted that there are few of these atoms for which, in the rHF case, it was difficult to infer from our numerical simulations whether the Fermi level is a slightly negative accidentally degenerate eigenvalue of the mean-field Hamiltonian, or whether the Fermi level is equal to zero. However, in the Xα case, atoms whose Fermi level is an accidentally degenerate eigenvalue of the mean-field Hamiltonian are clearly identified.

2. for atoms subjected to an external cylindrically-symmetric perturbative potential ($W \neq 0$):

   - we plot the variations of the density when the atom is subjected to an external uniform electric field ($W(\mathbf{r}) = -e_{\mathbf{z}} \cdot \mathbf{r}$, which is a *Stark* potential). For β small, we simply observe a polarization of the electronic cloud (recall that we solve the Kohn-Sham equations in a large ball with Dirichlet boundary conditions), while as β increases, we observe boundary effects: part of the electronic cloud is localized in the region where the external potential takes highly negative values;
   - we extract the first-order perturbation of the ground state density matrix in the case when $W(\mathbf{r}) = -e_{\mathbf{z}} \cdot \mathbf{r}$. Note that for such a potential W, (1.30) has no ground state; however, the first-order perturbation is well defined [25].

Chapter 2

A mathematical perspective on density functional perturbation theory

The content of this chapter is an article published in *Nonlinearity* [23], complemented with an appendix on second order perturbation theory. The article is devoted to analytic density functional perturbation theory. We first introduce the reduced Hartree-Fock model and explain the distinction between the non-degenerate and the degenerate case. Some conditions which insure the uniqueness of the reference density matrix (the ground state of the rHF unperturbed energy functional) are stated and proved. Then a perturbation potential is added to the energy functional. The aim of this contribution is to understand the influence of this potential on the energy and the ground state density matrix. The basic results in the non-degenerate case are recalled, mainly the existence, uniqueness and analyticity of the perturbed density matrix with respect to the perturbation. Moreover, a recursion formula is stated to calculate the coefficients of the perturbation expansion. The heart of this paper is the extension of those results to the degenerate case. Under some conditions, we were able to recover similar results as in the non-degenerate case: the perturbed ground state density matrix exists, is unique and analytic in the perturbation. Also, a recursion formula is found to compute the coefficients of the Rayleigh-Schrödinger series. The approach described in this chapter can be applied to other quantum mean-field models, such as the Kohn-Sham LDA model (under some additional assumptions). Finally, rigorous proofs of Wigner's $(2n+1)$-rule are provided.

2.1 Introduction

Eigenvalue perturbation theory has a long history. Introduced by Rayleigh [67] in the 1870's, it was used for the first time in quantum mechanics in an article by Schrödinger [74] published in 1926. The mathematical study of the perturbation theory of self-adjoint operators was initiated by Rellich [70] in 1937, and has been since then the matter of a large number of contributions in the mathematical literature (see [47, 71, 78] and references therein).

Perturbation theory plays a key role in quantum chemistry, where it is used in particular to compute the response properties of molecular systems to external electromagnetic fields (polarizability, hyperpolarizability, magnetic susceptibility, NMR shielding tensor, optical rotation, ...). Unless the number N of electrons in the molecular system under study is very small, it is not possible to solve numerically the $3N$-dimensional electronic Schrödinger equation. In the commonly used Hartree-Fock and Kohn-Sham models, the *linear* $3N$-*dimensional* electronic Schrödinger equation is approximated by a coupled system of N *nonlinear* 3-*dimensional* Schrödinger equations. The adaptation of the standard linear perturbation theory to the nonlinear setting of the Hartree-Fock model is called Coupled-Perturbed Hartree-Fock theory (CPHF) in the chemistry literature [59] (see also [21] for a mathematical analysis). Its adaptation to the Kohn-Sham model is usually referred to as the Density Functional Perturbation Theory (DFPT) [7, 40]. The term Coupled-Perturbed Kohn-Sham theory is also sometimes used.

The purpose of this article is to study, within the reduced Hartree-Fock (rHF) framework, the perturbations of the ground state energy, the ground state density matrix, and the ground state density of a molecular system, when a "small" external potential is turned on.

In the case when the Fermi level $\epsilon_{\rm F}^0$ is not a degenerate eigenvalue of the mean-field Hamiltonian (see Section 2.2 for a precise definition of these objects), the formalism of DFPT is well-known (see e.g. [28]). It has been used a huge number of publications in chemistry and physics, as well as in a few mathematical publications, e.g. [22, 29]. On the other hand, the degenerate case has not been considered yet, to the best of our knowledge. An interesting feature of DFPT in the degenerate case is that, in contrast with the usual situation in linear perturbation theory, the perturbation does not, in general, split the degenerate eigenvalue; it shifts the Fermi level and modifies the natural occupation numbers at the Fermi level.

The article is organized as follows. In Section 2.2, we recall the basic properties of rHF ground states and establish some new results on the uniqueness of the ground state density matrix for a few special cases. The classical results of DFPT in the non-degenerate case are recalled in Section 2.3, and a simple proof of Wigner's $(2n+1)$ rule is provided. This very important rule for applications allows one to compute the perturbation of the energy at the $(2n+1)^{\rm st}$ order from the perturbation of the density matrix at the $n^{\rm th}$ order only. In particular, the atomic forces (first-order perturbations of the energy) can be computed from the unperturbed density matrix (Wigner's rule for $n=0$), while hyperpolarizabilities of molecules (second and third-order perturbations of the energy) can be computed from the first-order perturbation of the density matrix (Wigner's rule for $n=1$). In Section 2.4, we investigate the situation when the Fermi level is a degenerate eigenvalue of the rHF Hamiltonian. We establish all our results in the rHF framework in the whole space

$\mathbb{R}^3$, for a local potential W with finite Coulomb energy. Extensions to other frameworks (Hartree-Fock and Kohn-Sham models, supercell with periodic boundary conditions, non-local potentials, Stark external potentials, ...) are discussed in Section 2.5. The proofs of the technical results are postponed until Section 2.6.

2.2 Some properties of the rHF model

Throughout this article, we consider a reference (unperturbed) system of N electrons subjected to an external potential V. For a molecular system containing M nuclei, V is given by

$$\forall x \in \mathbb{R}^3, \quad V(x) = -\sum_{k=1}^{M} z_k v(x - R_k),$$

where $z_k \in \mathbb{N}^*$ is the charge (in atomic units) and $R_k \in \mathbb{R}^3$ the position of the k^{th} nucleus. For point nuclei $v = |\cdot|^{-1}$, while for smeared nuclei $v = \mu \star |\cdot|^{-1}$, where $\mu \in C_{\rm c}^\infty(\mathbb{R}^3)$ is a non-negative radial function such that $\int_{\mathbb{R}^3} \mu = 1$.

In the framework of the (extended) Kohn-Sham model [28], the ground state energy of this reference system is obtained by minimizing an energy functional of the form

$$E^{\rm KS}(\gamma) := \mathrm{Tr}\left(-\frac{1}{2}\Delta\gamma\right) + \int_{\mathbb{R}^3} \rho_\gamma V + \frac{1}{2} D(\rho_\gamma, \rho_\gamma) + E^{\rm xc}(\rho_\gamma) \tag{2.1}$$

over the set

$$\mathcal{K}_N := \left\{\gamma \in \mathcal{S}(L^2(\mathbb{R}^3)) \mid 0 \le \gamma \le 1,\ \mathrm{Tr}\,(\gamma) = N,\ \mathrm{Tr}\,(-\Delta\gamma) < \infty\right\}$$

of the admissible one-body density matrices. To simplify the notation, we omit the spin variable. In the above definition, $\mathcal{S}(L^2(\mathbb{R}^3))$ denotes the space of the bounded self-adjoint operators on $L^2(\mathbb{R}^3)$, $0 \le \gamma \le 1$ means that the spectrum of γ is included in the range $[0, 1]$, and $\mathrm{Tr}\,(-\Delta\gamma)$ is the usual notation for $\mathrm{Tr}\,(|\nabla|\gamma|\nabla|)$, where $|\nabla| := (-\Delta)^{1/2}$ is the square root of the positive self-adjoint operator $-\Delta$ on $L^2(\mathbb{R}^3)$. The function $\rho_\gamma : \mathbb{R}^3 \to \mathbb{R}_+$ is the electronic density associated with the density matrix γ. Loosely speaking, $\rho_\gamma(x) = \gamma(x, x)$, where $\gamma(x, y)$ is the kernel of the operator γ. It holds

$$\rho_\gamma \ge 0, \quad \int_{\mathbb{R}^3} \rho_\gamma = N, \quad \int_{\mathbb{R}^3} |\nabla\sqrt{\rho_\gamma}|^2 \le \mathrm{Tr}\,(-\Delta\gamma)$$

(Hoffmann-Ostenhof inequality [52]) so that, in particular, $\rho_\gamma \in L^1(\mathbb{R}^3) \cap L^3(\mathbb{R}^3)$. The first term in the right-hand side of (2.1) is the Kohn-Sham kinetic energy functional, the second one models the interaction of the electrons with the external potential V, $D(\cdot, \cdot)$ is the Coulomb energy functional defined on $L^{6/5}(\mathbb{R}^3) \times L^{6/5}(\mathbb{R}^3)$ by

$$D(f, g) := \int_{\mathbb{R}^3} \int_{\mathbb{R}^3} \frac{f(x)\, g(y)}{|x - y|}\, dx\, dy,$$

and $E^{\rm xc}$ is the exchange-correlation functional. In the reduced Hartree-Fock (rHF) model (also sometimes called the Hartree model), the latter functional is taken identically equal to zero. In the Local Density Approximation (LDA), it is chosen equal to

$$E^{\rm xc}_{\rm LDA}(\rho) := \int_{\mathbb{R}^3} e_{\rm xc}(\rho(x))\, dx, \tag{2.2}$$

where the function $e_{\rm xc} : \mathbb{R}_+ \mapsto \mathbb{R}_-$ is such that for all $\overline{\rho} \in \mathbb{R}_+$, the non-positive number $e_{\rm xc}(\overline{\rho})$ is (an approximation of) the exchange-correlation energy density of the homogeneous electron gas with constant density $\overline{\rho}$. It is known that for neutral or positively charged molecular systems, that is when $Z = \sum_{k=1}^M z_k \geq N$, the minimization problem

$$E_0 := \inf \left\{ E^{\rm KS}(\gamma),\ \gamma \in \mathcal{K}_N \right\}, \tag{2.3}$$

has a ground state γ_0, for the rHF model [81] ($E^{\rm xc} = 0$), as well as for the Kohn-Sham LDA model [1] ($E^{\rm xc} = E^{\rm xc}_{\rm LDA}$).

This contribution aims at studying, in the rHF setting, the perturbations of the ground state energy E_0, of the ground state density matrix γ_0, and of the ground state density $\rho_0 = \rho_{\gamma_0}$ induced by an external potential W. In order to deal with both the unperturbed and the perturbed problem using the same formalism, we introduce the functional

$$E^{\rm rHF}(\gamma, W) := {\rm Tr}\left(-\frac{1}{2}\Delta\gamma\right) + \int_{\mathbb{R}^3} \rho_\gamma V + \frac{1}{2} D(\rho_\gamma, \rho_\gamma) + \int_{\mathbb{R}^3} \rho_\gamma W,$$

and the minimization problem

$$\mathcal{E}^{\rm rHF}(W) := \inf \left\{ E^{\rm rHF}(\gamma, W),\ \gamma \in \mathcal{K}_N \right\}. \tag{2.4}$$

We restrict ourselves to a potential W belonging to the space

$$\mathcal{C}' := \left\{ v \in L^6(\mathbb{R}^3) \mid \nabla v \in (L^2(\mathbb{R}^3))^3 \right\},$$

which can be identified with the dual of the Coulomb space

$$\mathcal{C} := \left\{ \rho \in \mathcal{S}'(\mathbb{R}^3) \,|\, \widehat{\rho} \in L^1_{\rm loc}(\mathbb{R}^3),\ |\cdot|^{-1}\widehat{\rho} \in L^2(\mathbb{R}^3) \right\}$$

of the charge distributions with finite Coulomb energy. Here, $\mathcal{S}'(\mathbb{R}^3)$ is the space of tempered distributions on $\mathbb{R}^3$ and $\widehat{\rho}$ is the Fourier transform of ρ (we use the normalization condition for which the Fourier transform is an isometry of $L^2(\mathbb{R}^3)$). When $W \in \mathcal{C}'$, the last term of the energy functional should be interpreted as

$$\int_{\mathbb{R}^3} \rho_\gamma W = \int_{\mathbb{R}^3} \overline{\widehat{\rho_\gamma}(k)}\, \widehat{W}(k)\, dk.$$

The right-hand side of the above equation is well-defined as the functions $k \mapsto |k|^{-1}\widehat{\rho}_\gamma(k)$ and $k \mapsto |k|\widehat{W}(k)$ are both in $L^2(\mathbb{R}^3)$, since $\rho_\gamma \in L^1(\mathbb{R}^3) \cap L^3(\mathbb{R}^3) \subset L^{6/5}(\mathbb{R}^3) \subset \mathcal{C}$.

The reference, unperturbed, ground state is obtained by solving (2.4) with $W = 0$.

Theorem 1 (unperturbed ground state for the rHF model [81])**.** *If*

$$Z = \sum_{k=1}^M z_k \geq N \qquad \textit{(neutral or positively charged molecular system)}, \tag{2.5}$$

then (2.4) has a ground state for $W = 0$, and all the ground states share the same density ρ_0. The mean-field Hamiltonian

$$H_0 := -\frac{1}{2}\Delta + V + \rho_0 \star |\cdot|^{-1},$$

is a self-adjoint operator on $L^2(\mathbb{R}^3)$ *and any ground state* γ_0 *is of the form*

$$\gamma_0 = \mathbb{1}_{(-\infty,\epsilon_{\rm F}^0)}(H_0) + \delta_0, \tag{2.6}$$

with $\epsilon_{\rm F}^0 \leq 0$, $0 \leq \delta_0 \leq 1$, $\mathrm{Ran}(\delta_0) \subset \mathrm{Ker}(H_0 - \epsilon_{\rm F}^0)$.

The real number $\epsilon_{\rm F}^0$, called the Fermi level, can be interpreted as the Lagrange multiplier of the constraint $\mathrm{Tr}\,(\gamma) = N$. The Hamiltonian H_0 is a self-adjoint operator on $L^2(\mathbb{R}^3)$ with domain $H^2(\mathbb{R}^3)$ and form domain $H^1(\mathbb{R}^3)$. Its essential spectrum is the range $[0, +\infty)$ and it possesses at least N non-positive eigenvalues, counting multiplicities. For each $j \in \mathbb{N}^*$, we set

$$\epsilon_j := \inf_{X_j \subset \mathcal{X}_j} \sup_{v \in X_j,\, \|v\|_{L^2}=1} \langle v|H_0|v\rangle,$$

where $\mathcal{X}_j$ is the set of the vector subspaces of $H^1(\mathbb{R}^3)$ of dimension j, and $v \mapsto \langle v|H_0|v\rangle$ the quadratic form associated with H_0. Recall (see e.g. [69, Section XIII.1]) that $(\epsilon_j)_{j\in\mathbb{N}^*}$ is a non-decreasing sequence of real numbers converging to zero, and that, if ϵ_j is negative, then H_0 possesses at least j negative eigenvalues (counting multiplicities) and ϵ_j is the $j^{\rm th}$ eigenvalue of H_0. We denote by $\phi_1^0, \phi_2^0, \cdots$ an orthonormal family of eigenvectors associated with the non-positive eigenvalues $\epsilon_1 \leq \epsilon_2 \leq \cdots$ of H_0. Three situations can *a priori* be encountered:

- **Case 1 (non-degenerate case):**

  $$H_0 \text{ has at least } N \text{ negative eigenvalues and } \epsilon_N < \epsilon_{N+1} \leq 0. \tag{2.7}$$

  In this case, the Fermi level $\epsilon_{\rm F}^0$ can be chosen equal to any real number in the range $(\epsilon_N, \epsilon_{N+1})$ and the ground state γ_0 is unique:

  $$\gamma_0 = \mathbb{1}_{(-\infty,\epsilon_{\rm F}^0)}(H_{\rho_0}) = \sum_{i=1}^{N} |\phi_i^0\rangle\langle\phi_i^0|;$$

- **Case 2 (degenerate case):**

  $$H_0 \text{ has at least } N+1 \text{ negative eigenvalues and } \epsilon_{N+1} = \epsilon_N. \tag{2.8}$$

  In this case, $\epsilon_{\rm F}^0 = \epsilon_N = \epsilon_{N+1} < 0$;

- **Case 3 (singular case):** $\epsilon_{\rm F}^0 = \epsilon_N = 0$.

In the non-degenerate case, problem (2.4), for $W \in \mathcal{C}'$ small enough, falls into the scope of the usual perturbation theory of nonlinear mean-field models dealt with in Section 2.3. The main purpose of this article is to extend the perturbation theory to the degenerate case. We will leave aside the singular case $\epsilon_N = 0$. It should be emphasized that the terminology *degenerate vs non-degenerate* used throughout this article refers to the possible degeneracy of the Fermi level, that is of a specific eigenvalue of the unperturbed mean-field Hamiltonian H_{ρ_0}, not to the possible degeneracy of the Hessian of the unperturbed energy functional at γ_0. The perturbation method heavily relies on the uniqueness of the ground state density matrix γ_0 and on the invertibility of the Hessian (or more precisely of a

reduced Hessian taking the constraints into account). In the non-degenerate case (Case 1), the minimizer γ_0 is unique and the reduced Hessian is always invertible. We will see that the same holds true in the degenerate case (Case 2) under assumption (2.9) below. We denote by

$$N_{\rm f} := \mathrm{Rank}\left(\mathbb{1}_{(-\infty,\epsilon_{\rm F}^0)}(H_0)\right)$$

the number of (fully occupied) eigenvalues lower than $\epsilon_{\rm F}^0$, and by

$$N_{\rm p} := \mathrm{Rank}\left(\mathbb{1}_{\{\epsilon_{\rm F}^0\}}(H_0)\right)$$

the number of (partially occupied) bound states of H_0 with energy $\epsilon_{\rm F}^0$. We also denote by $\mathbb{R}_{\rm S}^{N_{\rm p}\times N_{\rm p}}$ the space of real symmetric matrices of size $N_{\rm p}\times N_{\rm p}$.

Lemma 2. *Assume that (2.5) and (2.8) are satisfied. If for any $M \in \mathbb{R}_{\rm S}^{N_{\rm p}\times N_{\rm p}}$,*

$$\left(\forall x\in\mathbb{R}^3,\ \sum_{i,j=1}^{N_{\rm p}} M_{ij}\phi_{N_{\rm f}+i}^0(x)\phi_{N_{\rm f}+j}^0(x) = 0\right)\ \Rightarrow\ M = 0, \tag{2.9}$$

then the ground state γ_0 of (2.4) for $W = 0$ is unique

The sufficient condition (2.9) is satisfied in the following cases.

Proposition 3. *Assume that (2.5) and (2.8) are satisfied. If at least one of the two conditions below is fulfilled:*

1. *$N_{\rm p} \le 3$,*
2. *the external potential V is radial and the degeneracy of $\epsilon_{\rm F}^0$ is essential,*

then (2.9) holds true, and the ground state γ_0 of (2.4) for $W = 0$ is therefore unique.

Let us clarify the meaning of the second condition in Proposition 3. When V is radial, the ground state density is radial, so that H_0 is a Schrödinger operator with radial potential:

$$H_0 = -\frac{1}{2}\Delta + v(|x|).$$

It is well-known (see e.g. [69, Section XIII.3.B]) that all the eigenvalues of H_0 can be obtained by computing the eigenvalues of the one-dimensional Hamiltonians $h_{0,l}$, $l\in\mathbb{N}$, where $h_{0,l}$ is the self-adjoint operator on $L^2(0,+\infty)$ with domain $H^2(0,+\infty)\cap H_0^1(0,+\infty)$ defined by

$$h_{0,l} := -\frac{1}{2}\frac{d^2}{dr^2} + \frac{l(l+1)}{2r^2} + v(r).$$

If $\epsilon_{\rm F}^0$ is an eigenvalue of $h_{0,l}$, then its multiplicity, as an eigenvalue of H_0, is at least $2l+1$. It is therefore degenerate as soon as $l\ge 1$. If $\epsilon_{\rm F}^0$ is an eigenvalue of no other $h_{0,l'}$, $l'\neq l$, then its multiplicity is exactly $2l+1$, and the degeneracy is called essential. Otherwise, the degeneracy is called accidental. It is well-known that for the very special case when $v(r) = -Zr^{-1}$ (hydrogen-like atom), accidental degeneracy occurs at every eigenvalue but the lowest one, which is non-degenerate. On the other hand, this phenomenon is really exceptional, and numerical simulations seem to show that, as expected, there is no accidental degeneracy at the Fermi level when v is equal to the rHF mean-field potential of most atoms of the periodic table (see Chapter 4).

2.3 Density functional perturbation theory (non-degenerate case)

We denote by $\mathcal{B}(X,Y)$ the space of bounded linear operators from the Banach space X to the Banach space Y (with, as usual, $\mathcal{B}(X) := \mathcal{B}(X,X)$), by $\mathcal{S}(X)$ the space of self-adjoint operators on the Hilbert space X, by $\mathfrak{S}_1$ the space of trace class operators on $L^2(\mathbb{R}^3)$, and by $\mathfrak{S}_2$ the space of Hilbert-Schmidt operators on $L^2(\mathbb{R}^3)$ (all these spaces being endowed with their usual norms [68, 76]). We also introduce the Banach space

$$\mathfrak{S}_{1,1} := \{T \in \mathfrak{S}_1 \mid |\nabla|T|\nabla| \in \mathfrak{S}_1\},$$

with norm

$$\|T\|_{\mathfrak{S}_{1,1}} := \|T\|_{\mathfrak{S}_1} + \||\nabla\,|T|\nabla|\,\|_{\mathfrak{S}_1}.$$

We denote by $B_\eta(\mathcal{H})$ the open ball with center 0 and radius $\eta > 0$ of the Hilbert space $\mathcal{H}$.

Let us recall that in the non-degenerate case,

$$\gamma_0 \in \mathcal{P}_N := \left\{\gamma \in \mathcal{S}(L^2(\mathbb{R}^3)) \mid \gamma^2 = \gamma,\ \mathrm{Tr}\,(\gamma) = N,\ \mathrm{Tr}\,(-\Delta\gamma) < \infty\right\},$$

that is γ_0 is a rank-N orthogonal projector on $L^2(\mathbb{R}^3)$ with range in $H^1(\mathbb{R}^3)$, and

$$\gamma_0 = \mathbb{1}_{(-\infty,\epsilon_{\mathrm{F}}^0]}(H_0) = \frac{1}{2i\pi}\oint_{\mathscr{C}} (z - H_0)^{-1}\,dz,$$

where $\mathscr{C}$ is (for instance) the circle of the complex plane symmetric with respect to the real axis and intersecting it at points $\epsilon_1 - 1$ and ϵ_{F}^0.

2.3.1 Density matrix formulation

The linear and multilinear maps introduced in the following lemma will be useful to write down the Rayleigh-Schrödinger expansions in compact forms.

Lemma 4. *Assume that (2.5) and (2.7) are satisfied.*

1. *For each $k \in \mathbb{N}^*$, the k-linear map*

$$\begin{array}{rccl} Q^{(k)}: & (\mathcal{C}')^k & \to & \mathfrak{S}_{1,1} \\ & (v_1,\cdots,v_k) & \mapsto & \dfrac{1}{2i\pi}\displaystyle\oint_{\mathscr{C}} (z-H_0)^{-1}v_1(z-H_0)^{-1}v_2\cdots(z-H_0)^{-1}v_k(z-H_0)^{-1}\,dz \end{array}$$

is well-defined and continuous.

$\mathrm{Rank}(Q^{(k)}(v_1,\cdots,v_k)) \le N$ and $\mathrm{Tr}\,(Q^{(k)}(v_1,\cdots,v_k)) = 0$, for all $(v_1,\cdots,v_k) \in (\mathcal{C}')^k$, and there exists $0 < \alpha, C < \infty$ such that for all $k \in \mathbb{N}^*$ and all $(v_1,\cdots,v_k) \in (\mathcal{C}')^k$,

$$\|Q^{(k)}(v_1,\cdots,v_k)\|_{\mathfrak{S}_{1,1}} \le C\alpha^k \|v_1\|_{\mathcal{C}'}\cdots\|v_k\|_{\mathcal{C}'}. \tag{2.10}$$

2. *The linear map*

$$\begin{aligned} \mathcal{L} : \mathcal{C} &\to \mathcal{C} \\ \rho &\mapsto -\rho_{Q^{(1)}(\rho\star|\cdot|^{-1})}, \end{aligned}$$

associating to a charge density $\rho \in \mathcal{C}$, minus the density $\rho_{Q^{(1)}(\rho\star|\cdot|^{-1})}$ of the trace-class operator $Q^{(1)}(\rho\star|\cdot|^{-1})$, is a bounded positive self-adjoint operator on $\mathcal{C}$. As a consequence, $(1+\mathcal{L})$ is an invertible bounded positive self-adjoint operator on $\mathcal{C}$.

The main results of non-degenerate rHF perturbation theory for finite systems are gathered in the following theorem.

Theorem 5 (rHF perturbation theory in the non-degenerate case)**.** *Assume that (2.5) and (2.7) are satisfied. Then, there exists $\eta > 0$ such that*

1. *for all $W \in B_\eta(\mathcal{C}')$, (2.4) has a unique minimizer γ_W. In addition, $\gamma_W \in \mathcal{P}_N$ and*

$$\gamma_W = \mathbb{1}_{(-\infty,\epsilon_{\rm F}^0]}(H_W) = \frac{1}{2i\pi}\oint_{\mathscr{C}} (z - H_W)^{-1}\,dz, \tag{2.11}$$

where

$$H_W = -\frac{1}{2}\Delta + V + \rho_W \star |\cdot|^{-1} + W,$$

ρ_W being the density of γ_W;

2. *the mappings $W \mapsto \gamma_W$, $W \mapsto \rho_W$ and $W \mapsto \mathcal{E}^{\rm rHF}(W)$ are real analytic from $B_\eta(\mathcal{C}')$ into $\mathfrak{S}_{1,1}$, $\mathcal{C}$ and $\mathbb{R}$ respectively;*

3. *for all $W \in \mathcal{C}'$ and all $-\eta\|W\|_{\mathcal{C}'}^{-1} < \beta < \eta\|W\|_{\mathcal{C}'}^{-1}$,*

$$\gamma_{\beta W} = \gamma_0 + \sum_{k=1}^{+\infty} \beta^k \gamma_W^{(k)}, \quad \rho_{\beta W} = \rho_0 + \sum_{k=1}^{+\infty} \beta^k \rho_W^{(k)}, \quad \mathcal{E}^{\rm rHF}(\beta W) = \mathcal{E}(0) + \sum_{k=1}^{+\infty} \beta^k \mathcal{E}_W^{(k)},$$

the series being normally convergent in $\mathfrak{S}_{1,1}$, $\mathcal{C}$ and $\mathbb{R}$ respectively;

4. *denoting by $W^{(1)} = W + \rho_W^{(1)} \star |\cdot|^{-1}$ and $W^{(k)} = \rho_W^{(k)} \star |\cdot|^{-1}$ for $k \geq 2$, the coefficients $\rho_W^{(k)}$ of the expansion of $\rho_{\beta W}$ can be obtained by the recursion relation*

$$(1+\mathcal{L})\rho_W^{(k)} = \widetilde{\rho}_W^{(k)}, \tag{2.12}$$

where $\widetilde{\rho}_W^{(k)}$ is the density of the operator $\widetilde{Q}_W^{(k)}$ defined by

$$\begin{aligned} &\widetilde{Q}_W^{(1)} = Q^{(1)}(W), \\ &\forall k \geq 2, \quad \widetilde{Q}_W^{(k)} = \textstyle\sum_{l=2}^{k} \sum_{\substack{1 \leq j_1, \cdots, j_l \leq k-1, \\ \sum_{i=1}^{l} j_i = k}} Q^{(l)}(W^{(j_1)}, \cdots, W^{(j_l)}); \end{aligned} \tag{2.13}$$

5. *the coefficients $\gamma_W^{(k)}$ and $\mathcal{E}_W^{(k)}$ are then given by*

$$\gamma_W^{(k)} = \frac{1}{2i\pi}\oint_{\mathscr{C}} (z - H_0)^{-1} W^{(k)} (z - H_0)^{-1}\,dz + \widetilde{Q}_W^{(k)}, \tag{2.14}$$

and

$$\mathcal{E}_W^{(k)} = \mathrm{Tr}\left(H_0 \gamma_W^{(k)}\right) + \frac{1}{2}\sum_{l=1}^{k-1} D\left(\rho_W^{(l)}, \rho_W^{(k-l)}\right) + \int_{\mathbb{R}^3} \rho_W^{(k-1)}\, W. \tag{2.15}$$

2.3.2 Molecular orbital formulation

When $\epsilon_1 < \epsilon_2 < \cdots < \epsilon_N < \epsilon_{\rm F}^0$, that is when the lowest N eigenvalues of H_0 are all non-degenerate, it can be seen, following the same lines as in [21], that, for all $W \in \mathcal{C}'$, there exist real analytic functions $\beta \mapsto \epsilon_{W,i}(\beta) \in \mathbb{R}$ and $\beta \mapsto \phi_{W,i}(\beta) \in H^2(\mathbb{R}^3)$ defined in the neighborhood of 0 such that $\epsilon_{W,i}(0) = \epsilon_i$, $\phi_{W,i}(0) = \phi_i^0$, and

$$\begin{cases} H_{\beta W}\phi_{W,i}(\beta) = \epsilon_{W,i}(\beta)\phi_{W,i}(\beta), \\ (\phi_{W,i}(\beta), \phi_{W,j}(\beta))_{L^2} = \delta_{ij}, \\ \epsilon_{W,1}(\beta) < \epsilon_{W,2}(\beta) < \cdots < \epsilon_{W,N}(\beta) \text{ are the lowest eigenvalues of } H_{\beta W} \text{ (counting multiplicities).} \end{cases}$$

The coefficients of the Rayleigh-Schrödinger expansions

$$\epsilon_{W,i}(\beta) = \sum_{k=0}^{+\infty} \beta^k \epsilon_{W,i}^{(k)}, \qquad \phi_{W,i}(\beta) = \sum_{k=0}^{+\infty} \beta^k \phi_{W,i}^{(k)},$$

where $\epsilon_{W,i}^0 = \epsilon_i$ and $\phi_{W,i}^0 = \phi_i^0$, are obtained by solving the system

$$\forall k \in \mathbb{N}^*, \quad \forall 1 \le i \le N, \qquad \begin{cases} (H_0 - \epsilon_i)\,\phi_{W,i}^{(k)} + \sum_{j=1}^N K_{ij}^0 \phi_{W,j}^{(k)} = f_{W,i}^{(k)} + \epsilon_{W,i}^{(k)}\phi_i^0, \\ \int_{\mathbb{R}^3} \phi_{W,i}^{(k)}\phi_i^0 = \alpha_{W,i}^{(k)}, \end{cases} \tag{2.16}$$

where

$$\forall \phi \in L^2(\mathbb{R}^3), \quad K_{ij}^0\phi = 2\left(\phi_j^0\phi \star |\cdot|^{-1}\right)\phi_i^0,$$

and where the right-hand sides

$$f_{W,i}^{(k)} = -W\phi_{W,i}^{(k-1)} - \sum_{j=1}^N \sum_{\substack{1 \le l_1, l_2, l_3 \le k-1, \\ l_1+l_2+l_3 = k}} \left(\phi_{W,j}^{(l_1)}\phi_{W,j}^{(l_2)} \star |\cdot|^{-1}\right)\phi_{W,i}^{(l_3)} + \sum_{l=1}^{k-1} \epsilon_{W,i}^{(l)}\phi_{W,i}^{(k-l)},$$

and

$$\alpha_{W,i}^{(k)} = -\frac{1}{2}\sum_{l=1}^{k-1} \int_{\mathbb{R}^3} \phi_{W,i}^{(l)}\phi_{W,i}^{(k-l)}.$$

at order k only depend on the coefficients $\phi_{W,j}^{(l)}$ and $\epsilon_{W,j}^{(l)}$ at order $l \le k-1$. System (2.16) can therefore be considered as an infinite triangular system with respect to k.

The fact that all the terms of the Rayleigh-Schrödinger series are defined unambiguously by (2.16) is guaranteed by the following lemma and the fact that for all ϕ and ψ in $H^1(\mathbb{R}^3)$, $W\phi \in H^{-1}(\mathbb{R}^3)$ and $\phi\psi \star |\cdot|^{-1} \in L^\infty(\mathbb{R}^3)$.

Lemma 6. *Assume that (2.5) and (2.7) are satisfied and that $\epsilon_1 < \epsilon_2 < \cdots < \epsilon_N < \epsilon_{\rm F}^0$. For all $f = (f_1, \cdots, f_N) \in (H^{-1}(\mathbb{R}^3))^N$ and all $\alpha = (\alpha_1, \cdots, \alpha_N) \in \mathbb{R}^N$, the linear problem*

$$\forall 1 \le i \le N, \qquad \begin{cases} (H_0 - \epsilon_i)\,\psi_i + \sum_{j=1}^N K_{ij}^0\psi_j = f_i + \eta_i\phi_i^0, \\ \int_{\mathbb{R}^3} \psi_i\phi_i^0 = \alpha_i, \end{cases} \tag{2.17}$$

has a unique solution $(\Psi, \eta) = ((\psi_1, \cdots, \psi_N), (\eta_1, \cdots, \eta_N))$ in $(H^1(\mathbb{R}^3))^N \times \mathbb{R}^N$. Moreover, if $f \in (L^2(\mathbb{R}^3))^N$, then $\Psi \in (H^2(\mathbb{R}^3))^N$.

Let us notice that, although the constraints $\int_{\mathbb{R}^3} \phi_{W,i}(\beta)\phi_{W,j}(\beta) = 0$ for $i \neq j$ are not explicitly taken into account in the formal derivation of (2.16), the unique solution to (2.16) is compatible with these constraints since it automatically satisfies

$$\forall k \in \mathbb{N}^*, \quad \forall 1 \leq i,j \leq N, \qquad \int_{\mathbb{R}^3} \sum_{l=0}^{k} \phi_{W,i}^{(l)} \phi_{W,j}^{(k-l)} = 0. \tag{2.18}$$

A proof of the above result is provided in Section 2.6.6, together with the proof of Lemma 6.

Let us finally mention that the Rayleigh-Schrödinger expansions of the density matrix $\gamma_{\beta W}$ and of the molecular orbitals $\phi_{W,i}(\beta)$ are related by

$$\gamma_W^{(k)} = \sum_{i=1}^{N} \sum_{l=0}^{k} |\phi_{W,i}^{(l)}\rangle\langle\phi_{W,i}^{(k-l)}|,$$

where we have used Dirac's bra-ket notation.

2.3.3 Wigner's $(2n+1)$-rule

According to (2.15), the first n coefficients of the Rayleigh-Schrödinger expansion of the density matrix allows one to compute the first n coefficients of the perturbation expansion of the energy. Wigner's $(2n+1)$-rule ensures that, in fact, they provide an approximation of the energy up to order $(2n+1)$. This property, which is very classical in linear perturbation theory, has been extended only recently to the nonlinear DFT framework [5]. In the present section, we complement the results established in [5] by providing a different, more general and compact proof, which also works in the infinite dimensional setting.

In the density matrix formulation, the Wigner's $(2n+1)$-rule can be formulated as follows. We introduce the nonlinear projector Π on $\mathcal{S}(L^2(\mathbb{R}^3))$ defined by

$$\forall T \in \mathcal{S}(L^2(\mathbb{R}^3)), \quad \Pi(T) = \mathbb{1}_{[1/2,+\infty)}(T),$$

and, for $W \in \mathcal{C}'$ and $\beta \in \mathbb{R}$, we denote by

$$\widetilde{\gamma}_W^{(n)}(\beta) := \Pi\left(\gamma_0 + \sum_{k=1}^{n} \beta^k \gamma_W^{(k)}\right).$$

For $T \in \mathcal{B}(L^2(\mathbb{R}^3))$, resp. $T \in \mathfrak{S}_2$, we denote by

$$\mathrm{dist}(T, \mathcal{P}_N) := \inf\left\{\|T-\gamma\|,\ \gamma \in \mathcal{P}_N\right\},$$

resp.

$$\mathrm{dist}_{\mathfrak{S}_2}(T, \mathcal{P}_N) := \inf\left\{\|T-\gamma\|_{\mathfrak{S}_2},\ \gamma \in \mathcal{P}_N\right\},$$

the distance from T to $\mathcal{P}_N$ for the operator, resp. Hilbert-Schmidt, norm. The projector Π enjoys the following properties.

Lemma 7. *For each $T \in \Omega := \left\{T \in \mathcal{S}(L^2(\mathbb{R}^3)) \mid \mathrm{dist}(T,\mathcal{P}_N) < 1/2,\ \mathrm{Ran}(T) \subset H^1(\mathbb{R}^3)\right\}$, $\Pi(T) \in \mathcal{P}_N$. Besides, for each $T \in \Omega \cap \mathfrak{S}_2$, $\Pi(T)$ is the unique solution to the variational problem*

$$\|T - \Pi(T)\|_{\mathfrak{S}_2} = \min_{\gamma \in \mathcal{P}_N} \|T-\gamma\|_{\mathfrak{S}_2} = \mathrm{dist}_{\mathfrak{S}_2}(T, \mathcal{P}_N). \tag{2.19}$$

It follows from Lemma 7 that, for all $W \in \mathcal{C}'$ and $|\beta|$ small enough, $\widetilde{\gamma}_W^{(n)}(\beta)$ is the projection on $\mathcal{P}_N$ (in the sense of (2.19)) of the Rayleigh-Schrödinger expansion of the density matrix up to order n.

Theorem 8 (Wigner's $(2n+1)$-rule in the non-degenerate case)**.** *Assume that (2.5) and (2.7) are satisfied. For each $n \in \mathbb{N}$ and all $W \in \mathcal{C}'$, it holds*

$$0 \leq E^{\mathrm{rHF}}(\widetilde{\gamma}_W^{(n)}(\beta), W) - \mathcal{E}^{\mathrm{rHF}}(\beta W) = \mathcal{O}(|\beta|^{2n+2}). \tag{2.20}$$

Note that as $\gamma_0 + \sum_{k=1}^n \beta^k \gamma_W^{(k)}$ has finite-rank N_n, it can be diagonalized in an orthonormal basis of $L^2(\mathbb{R}^3)$ as

$$\gamma_0 + \sum_{k=1}^{n} \beta^k \gamma_W^{(k)} = \sum_{i=1}^{N_n} g_{W,i}(\beta) |\widetilde{\phi}_{W,i}(\beta)\rangle\langle\widetilde{\phi}_{W,i}(\beta)|, \tag{2.21}$$

with $(\widetilde{\phi}_{W,i}(\beta), \widetilde{\phi}_{W,j}(\beta))_{L^2} = \delta_{ij}$, $g_{W,i}(\beta) \in \mathbb{R}$, and $|g_{W,i}(\beta)| \geq |g_{W,j}(\beta)|$ for all $i \leq j$. We also have

$$\sum_{i=1}^{N_n} g_{W,i}(\beta) = \mathrm{Tr}\left(\gamma_0 + \sum_{k=1}^{n} \beta^k \gamma_W^{(k)}\right) = N,$$

since, in view of (2.13), (2.14) and Lemma 4, $\mathrm{Tr}\,(\gamma_W^{(k)}) = 0$ for all $k \geq 1$. For $|\beta|$ small enough, the above operator is in Ω, and therefore, $g_{W,1}(\beta) \geq g_{W,2}(\beta) \geq \cdots \geq g_{W,N}(\beta) > 1/2$ and $|g_{W,j}(\beta)| < 1/2$ for all $j \geq N+1$. We then have

$$\widetilde{\gamma}_W^{(n)}(\beta) = \sum_{i=1}^{N} |\widetilde{\phi}_{W,i}(\beta)\rangle\langle\widetilde{\phi}_{W,i}(\beta)|. \tag{2.22}$$

2.4 Perturbations of the rHF model in the degenerate case

We consider in this section the degenerate case. We assume that (2.9) is satisfied, yielding that the ground state γ_0 of the unperturbed problem (2.4) with $W = 0$ is unique. We also make the following assumption:

$$\epsilon_{\mathrm{F}}^0 < 0, \quad \mathrm{Rank}(\delta_0) = N_{\mathrm{p}}, \quad \mathrm{Ker}(1 - \delta_0) = \{0\}\,, \tag{2.23}$$

where δ_0 is the operator in (2.6). Assumption (2.23) means that the natural occupation numbers at the Fermi level (or in other words the N_{p} eigenvalues of $\delta_0|_{\mathrm{Ker}(\mathrm{H}_0 - \epsilon_{\mathrm{F}}^0)}$) are strictly comprised between 0 and 1. As a consequence, γ_0 belongs to the subset

$$\mathcal{K}_{N_{\mathrm{f}},N_{\mathrm{p}}} := \{\gamma \in \mathcal{K}_N \mid \mathrm{Rank}(\gamma) = N_{\mathrm{f}} + N_{\mathrm{p}},\ \dim(\mathrm{Ker}(1-\gamma)) = N_{\mathrm{f}}\}$$

of $\mathcal{K}_N$.

We are going to prove that, under assumptions (2.9) and (2.23), the rHF problem (2.4) has a unique minimizer for $\|W\|_{\mathcal{C}'}$ small enough, which belongs to $\mathcal{K}_{N_{\mathrm{f}},N_{\mathrm{p}}}$ and whose dependence in W is real analytic. To establish those results and compute the perturbation expansion in W of the minimizer, we proceed as follow:

1. we first construct a real analytic local chart of $\mathcal{K}_{N_\mathrm{f},N_\mathrm{p}}$ in the vicinity of γ_0 (Section 2.4.1);

2. we use this local chart to prove that, for $\|W\|_{\mathcal{C}'}$ small enough, the minimization problem
$$\widetilde{\mathcal{E}}^{\mathrm{rHF}}(W) := \inf\left\{E^{\mathrm{rHF}}(\gamma, W),\ \gamma \in \mathcal{K}_{N_\mathrm{f},N_\mathrm{p}}\right\} \tag{2.24}$$
has a unique local minimizer γ_W in the vicinity of γ_0, and that the mappings $W \mapsto \gamma_W \in \mathfrak{S}_{1,1}$ and $W \mapsto \widetilde{\mathcal{E}}^{\mathrm{rHF}}(W)$ are real analytic; we then prove that γ_W is actually the unique global minimizer of (2.4) (Section 2.4.2), hence that $\widetilde{\mathcal{E}}^{\mathrm{rHF}}(W) = \mathcal{E}^{\mathrm{rHF}}(W)$;

3. we finally derive the coefficients of the Rayleigh-Schrödinger expansions of γ_W and $\mathcal{E}^{\mathrm{rHF}}(W)$, and prove that Wigner's $(2n+1)$-rule also holds true in the degenerate case (Section 2.4.3).

2.4.1 Parametrization of $\mathcal{K}_{N_\mathrm{f},N_\mathrm{p}}$ in the vicinity of γ_0

We first introduce the Hilbert spaces $\mathcal{H}_\mathrm{f} = \mathrm{Ran}(\mathbb{1}_{(-\infty,\epsilon_\mathrm{F}^0)}(H_0))$, $\mathcal{H}_\mathrm{p} = \mathrm{Ran}(\mathbb{1}_{\{\epsilon_\mathrm{F}^0\}}(H_0))$ and $\mathcal{H}_\mathrm{u} = \mathrm{Ran}(\mathbb{1}_{(\epsilon_\mathrm{F}^0,+\infty)}(H_0))$, corresponding respectively to the fully occupied, partially occupied, and unoccupied spaces of the unperturbed ground state density matrix γ_0. For later purpose, we also set $\mathcal{H}_\mathrm{o} = \mathcal{H}_\mathrm{f} \oplus \mathcal{H}_\mathrm{p}$. As
$$L^2(\mathbb{R}^3) = \mathcal{H}_\mathrm{f} \oplus \mathcal{H}_\mathrm{p} \oplus \mathcal{H}_\mathrm{u},$$
any linear operator T on $L^2(\mathbb{R}^3)$ can be written as a 3×3 block operator
$$T = \begin{bmatrix} T_\mathrm{ff} & T_\mathrm{fp} & T_\mathrm{fu} \\ T_\mathrm{pf} & T_\mathrm{pp} & T_\mathrm{pu} \\ T_\mathrm{uf} & T_\mathrm{up} & T_\mathrm{uu} \end{bmatrix},$$
where T_xy is a linear operator from $\mathcal{H}_\mathrm{y}$ to $\mathcal{H}_\mathrm{x}$. In particular, γ_0 and H_0 are block diagonal in this representation, and it holds
$$\gamma_0 = \begin{bmatrix} 1 & 0 & 0 \\ 0 & \Lambda & 0 \\ 0 & 0 & 0 \end{bmatrix}, \qquad H_0 = \begin{bmatrix} H_0^{--} & 0 & 0 \\ 0 & \epsilon_\mathrm{F}^0 & 0 \\ 0 & 0 & H_0^{++} \end{bmatrix}$$
with $0 \le \Lambda = \delta_0|_{\mathcal{H}_p} \le 1$, $H_0^{--} - \epsilon_\mathrm{F}^0 \le -g_- := \epsilon_{N_\mathrm{f}} - \epsilon_\mathrm{F}^0$ and $H_0^{++} - \epsilon_\mathrm{F}^0 \ge g_+ := \epsilon_{N_\mathrm{f}+N_\mathrm{p}+1} - \epsilon_\mathrm{F}^0$.

We then introduce

- the spaces of finite-rank operators
$$\mathcal{A}_\mathrm{ux} := \left\{A_\mathrm{ux} \in \mathcal{B}(\mathcal{H}_\mathrm{x}, \mathcal{H}_\mathrm{u}) \mid (H_0^{++} - \epsilon_\mathrm{F}^0)^{1/2} A_\mathrm{ux} \in \mathcal{B}(\mathcal{H}_\mathrm{x}, \mathcal{H}_\mathrm{u})\right\},$$
for $\mathrm{x} \in \{\mathrm{f}, \mathrm{p}\}$, endowed with the inner product
$$(A_\mathrm{ux}, B_\mathrm{ux})_{\mathcal{A}_\mathrm{ux}} := \mathrm{Tr}\,(A_\mathrm{ux}^*(H_0^{++} - \epsilon_\mathrm{F}^0)B_\mathrm{ux});$$

- the finite dimensional spaces
$$\mathcal{A}_{\rm pf} := \mathcal{B}(\mathcal{H}_{\rm f}, \mathcal{H}_{\rm p})$$
and
$$\mathcal{A}_{\rm pp} := \{A_{\rm pp} \in \mathcal{S}(\mathcal{H}_{\rm p}) \mid {\rm Tr}\,(A_{\rm pp}) = 0\};$$
- the product space
$$\mathcal{A} := \mathcal{A}_{\rm uf} \times \mathcal{A}_{\rm up} \times \mathcal{A}_{\rm pf} \times \mathcal{A}_{\rm pp},$$
which we endow with the inner product
$$(A, B)_{\mathcal{A}} = \sum_{\rm x\in\{f,p\}} (A_{\rm ux}, B_{\rm ux})_{\mathcal{A}_{\rm ux}} + \sum_{\rm x\in\{f,p\}} {\rm Tr}\,\left(A_{\rm px} B_{\rm px}^*\right).$$

To any $A = (A_{\rm uf}, A_{\rm up}, A_{\rm pf}, A_{\rm pp}) \in \mathcal{A}$, we associate the bounded linear operator $\Gamma(A)$ on $L^2(\mathbb{R}^3)$ defined as

$$\Gamma(A) := \exp\left(L_{\rm uo}(A)\right)\ \exp\left(L_{\rm pf}(A)\right)\ \left(\gamma_0 + L_{\rm pp}(A)\right)\ \exp\left(-L_{\rm pf}(A)\right)\ \exp\left(-L_{\rm uo}(A)\right), \tag{2.25}$$

where

$$L_{\rm uo}(A) := \begin{bmatrix} 0 & 0 & -A_{\rm uf}^* \\ 0 & 0 & -A_{\rm up}^* \\ A_{\rm uf} & A_{\rm up} & 0 \end{bmatrix}, \quad L_{\rm pf}(A) := \begin{bmatrix} 0 & -A_{\rm pf}^* & 0 \\ A_{\rm pf} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}, \quad L_{\rm pp}(A) := \begin{bmatrix} 0 & 0 & 0 \\ 0 & A_{\rm pp} & 0 \\ 0 & 0 & 0 \end{bmatrix}.$$

Note that Γ is real analytic from $\mathcal{A}$ to $\mathfrak{S}_{1,1}$, $\Gamma(0) = \gamma_0$, and $\Gamma(A) \in \mathcal{K}_N$ for all $A_{\rm pp}$ such that $0 \leq \Lambda + A_{\rm pp} \leq 1$. In addition, it follows from Assumption (2.23) that $\Gamma(A) \in \mathcal{K}_{N_{\rm f},N_{\rm p}}$ for all $A \in \mathcal{A}$ small enough. The following lemma provides the parametrization of $\mathcal{K}_{N_{\rm f},N_{\rm p}}$ near γ_0 our analysis is based upon.

Lemma 9. *Assume that (2.5), (2.8), (2.9) and (2.23) are satisfied. Then there exists an open neighborhood $\mathcal{O}$ of 0 in $\mathcal{A}$ and an open neighborhood $\mathcal{O}'$ of γ_0 in $\mathfrak{S}_{1,1}$ such that the real analytic mapping*
$$\begin{array}{ccc} \mathcal{O} & \to & \mathcal{K}_{N_{\rm f},N_{\rm p}} \cap \mathcal{O}' \\ A & \mapsto & \Gamma(A) \end{array} \tag{2.26}$$
is bijective.

In other words, the inverse of the above mapping is a local chart of $\mathcal{K}_{N_{\rm f},N_{\rm p}}$ in the vicinity of γ_0. Note that a similar, though not identical, parametrization of the finite-dimensional counterpart of $\mathcal{K}_{N_{\rm f},N_{\rm p}}$ obtained by discretization in atomic orbital basis sets, was used in [18] to design quadratically convergent self-consistent algorithms for the extended Kohn-Sham model.

2.4.2 Existence and uniqueness of the minimizer of (2.4) for W small enough

We now define the energy functional

$$E(A,W) := E^{\mathrm{rHF}}(\Gamma(A),W), \tag{2.27}$$

for all $A \in \mathcal{O}$ and all $W \in \mathcal{C}'$, which, in view of Lemma 9 allows us to study the existence and uniqueness of local minimizers of (2.24) in the vicinity of γ_0 when $\|W\|_{\mathcal{C}'}$ is small enough. The functional E is clearly real analytic; we denote by

$$F(A,W) := \nabla_A E(A,W), \tag{2.28}$$

the gradient of E with respect to A, evaluated at point (A,W). As γ_0 is the unique minimizer of the functional $\gamma \mapsto E^{\mathrm{rHF}}(\gamma,0)$ on $\mathcal{K}_N$, hence on $\mathcal{K}_{N_\mathrm{f},N_\mathrm{p}}$, 0 is the unique minimizer of the functional $A \mapsto E(A,0)$ on $\mathcal{O}$, so that

$$F(0,0) = 0.$$

Lemma 10. *Assume that (2.5), (2.8), (2.9) and (2.23) are satisfied. Let*

$$\Theta := \frac{1}{2} F'_A(0,0)|_{\mathcal{A}\times\{0\}},$$

where $F'_A(0,0)|_{\mathcal{A}\times\{0\}}$ is the restriction to the subspace $\mathcal{A}\times\{0\} \equiv \mathcal{A}$ of $\mathcal{A}\times\mathcal{C}'$ of the derivative of F with respect to A at $(0,0)$. The linear map Θ is a bicontinuous coercive isomorphism from $\mathcal{A}$ to its dual $\mathcal{A}'$.

We infer from Lemma 10 and the real analytic version of the implicit function theorem that for $W \in \mathcal{C}'$ small enough, the equation $F(A,W) = 0$ has a unique solution $\widetilde{A}(W)$ in $\mathcal{O}$, and that the function $W \mapsto \widetilde{A}(W)$ is real analytic in the neighborhood of 0. It readily follows from (2.28) and Lemma 9 that for $W \in \mathcal{C}'$ small enough,

$$\gamma_W := \Gamma(\widetilde{A}(W)) \tag{2.29}$$

is the unique critical point of (2.24) in the vicinity of γ_0. This critical point is in fact a local minimizer since Θ, which is in fact the second derivative of the energy functional $A \mapsto E(A,0)$, is coercive. We have actually the following much stronger result.

Lemma 11. *Assume that (2.5), (2.8), (2.9) and (2.23) are satisfied. Then, for $\|W\|_{\mathcal{C}'}$ small enough, the density matrix γ_W defined by (2.29) is the unique global minimizer of (2.4).*

We conclude this section by providing the explicit form of Θ, which is useful to prove Lemma 10, but also to compute the Rayleigh-Schrödinger expansion of γ_W:

$$\begin{aligned}
[\Theta(A)]_{\mathrm{uf}} &= -A_{\mathrm{uf}}(H_0^{--} - \epsilon_\mathrm{F}^0) + (H_0^{++} - \epsilon_\mathrm{F}^0)A_{\mathrm{uf}} + \frac{1}{2}[\mathcal{J}(A)]_{\mathrm{uf}},\\
[\Theta(A)]_{\mathrm{up}} &= (H_0^{++} - \epsilon_\mathrm{F}^0)A_{\mathrm{up}}\Lambda + \frac{1}{2}[\mathcal{J}(A)]_{\mathrm{up}},\\
[\Theta(A)]_{\mathrm{pf}} &= -(1-\Lambda)A_{\mathrm{pf}}\left(H_0^{--} - \epsilon_\mathrm{F}^0\right) + \frac{1}{2}[\mathcal{J}(A)]_{\mathrm{pf}},\\
[\Theta(A)]_{\mathrm{pp}} &= \frac{1}{2}[\mathcal{J}(A)]_{\mathrm{pp}},
\end{aligned}$$

$\mathcal{J}$ denoting the linear operator from $\mathcal{A}$ to $\mathcal{A}'$ defined by

$$\forall (A, A') \in \mathcal{A} \times \mathcal{A}, \quad \langle \mathcal{J}(A), A' \rangle = D(\rho_{\gamma_1(A)}, \rho_{\gamma_1(A')}),$$

where

$$\gamma_1(A) = \langle \Gamma'(0), A \rangle = [L_{\rm uo}(A) + L_{\rm pf}(A), \gamma_0] + L_{\rm pp}(A). \tag{2.30}$$

A key observation for the sequel is that

$$\forall A \in \mathcal{A}, \quad \text{Tr } (H_0 \gamma_1(A)) = 0. \tag{2.31}$$

2.4.3 Rayleigh-Schrödinger expansions

It immediately follows from the previous two sections that, for any $W \in \mathcal{C}'$, the functions $\beta \mapsto A_W(\beta) := \widetilde{A}(\beta W)$ and $\beta \mapsto \gamma_{\beta W} := \Gamma(\widetilde{A}(\beta W))$ are well-defined and real analytic in the vicinity of 0. The purpose of this section is to provide a method to compute the coefficients $A_W^{(k)}$, $\gamma_W^{(k)}$ and $\mathcal{E}_W^{(k)}$ of the expansions

$$A_W(\beta) = \sum_{k=1}^{+\infty} \beta^k A_W^{(k)}, \quad \gamma_{\beta W} = \gamma_0 + \sum_{k=1}^{+\infty} \beta^k \gamma_W^{(k)} \quad \text{and} \quad \mathcal{E}^{\rm rHF}(\beta W) = \mathcal{E}^{\rm rHF}(0) + \sum_{k=1}^{+\infty} \beta^k \mathcal{E}_W^{(k)}.$$

We can already notice that the coefficients $\gamma_W^{(k)}$ and $\mathcal{E}_W^{(k)}$ are easily deduced from the coefficients $A_W^{(k)}$. Using the following version of the Baker-Campbell-Hausdorff formula

$$e^X Y e^{-X} = Y + [X, Y] + \frac{1}{2!}[X, [X, Y]] + \frac{1}{3!}[X, [X, [X, Y]]] + ...,$$

we indeed obtain

$$\gamma_W^{(k)} = \sum_{1 \le l \le k} \sum_{\alpha \in (\mathbb{N}^*)^l \,|\, |\alpha|_1 = k} \gamma_{W,l}^{\alpha} \qquad \text{with} \qquad \gamma_{W,l}^{\alpha} = \gamma_l(A_W^{(\alpha_1)}, \cdots, A_W^{(\alpha_l)}), \tag{2.32}$$

where for all $\alpha = (\alpha_1, \cdots, \alpha_l) \in (\mathbb{N}^*)^l$, $|\alpha|_1 = \alpha_1 + \cdots + \alpha_l$, $|\alpha|_\infty = \max(\alpha_i)$, and

$$\begin{aligned} \gamma_l(A_1, \cdots, A_l) &= \sum_{i+j=l} \frac{1}{i!j!} [L_{\rm uo}(A_1), \cdots, [L_{\rm uo}(A_i), [L_{\rm pf}(A_{i+1}), \cdots, [L_{\rm pf}(A_l), \gamma_0] \cdots] \\ &+ \sum_{i+j=l-1} \frac{1}{i!j!} [L_{\rm uo}(A_1), ..., [L_{\rm uo}(A_i), [L_{\rm pf}(A_{i+1}), \cdots, [L_{\rm pf}(A_{l-1}), L_{\rm pp}(A_l)] \cdots], \end{aligned}$$

for all $(A_1, \cdots, A_l) \in \mathcal{A}^l$. Note that for $l = 1$, the above definition agrees with (2.30), and that, more generally,

$$\forall A \in \mathcal{A}, \quad \Gamma(A) = \gamma_0 + \sum_{l=1}^{+\infty} \gamma_l(A, \cdots, A). \tag{2.33}$$

It follows from (2.31) and (2.32) that

$$\mathcal{E}_W^{(1)} = \int_{\mathbb{R}^3} \rho_{\gamma_0} W, \tag{2.34}$$

and that for all $k \geq 2$,

$$\mathcal{E}_W^{(k)} = \mathrm{Tr}\left(-\frac{1}{2}\Delta\gamma_W^{(k)}\right) + \int_{\mathbb{R}^3} \rho_{\gamma_W^{(k)}} V + \frac{1}{2}\sum_{l=0}^{k} D\left(\rho_{\gamma_W^{(l)}}, \rho_{\gamma_W^{(k-l)}}\right) + \int_{\mathbb{R}^3} \rho_{\gamma_W^{(k-1)}} W \qquad (2.35)$$

We will see however that the above formula is far from being optimal, in the sense that $\mathcal{E}_W^{(k)}$ can be computed using the coefficients $A_W^{(j)}$ for $1 \leq j \leq k/2$ only (see formulation (2.39) of Wigner's $(2n+1)$-rule), whereas the direct evaluation of $\mathcal{E}_W^{(k)}$ based on (2.32) and (2.35) requires the knowledge of the $A_W^{(j)}$'s up to $j = k$.

2.4.4 Main results for the degenerate case

The following theorem collects the results obtained so far, and provides a systematic way to construct the $A_W^{(k)}$'s, as well as an extension to Wigner's $(2n+1)$-rule to the degenerate case.

Theorem 12. *Assume that (2.5), (2.8), (2.9) and (2.23) are satisfied. Then there exists $\eta > 0$, such that*

1. existence and uniqueness of the ground state: *for all $W \in B_\eta(\mathcal{C}')$, the rHF model (2.4) has a unique ground state γ_W;*

2. no energy level splitting at the Fermi level: *the mean-field Hamiltonian*

$$H_W = -\frac{1}{2}\Delta + V + \rho_W \star |\cdot|^{-1} + W$$

(where ρ_W is the density of γ_W) has at least $N_\mathrm{o} = N_\mathrm{f} + N_\mathrm{p}$ negative eigenvalues (counting multiplicities), the degeneracy of the $(N_\mathrm{f}+1)^{\mathrm{st}}$ eigenvalue, which is also the Fermi level ϵ_F^W of the system, being equal to N_p, and it holds

$$\gamma_W = \mathbb{1}_{(-\infty,\epsilon_\mathrm{F}^W)}(H_W) + \delta_W,$$

where $0 \leq \delta_W \leq 1$ is an operator such that $\mathrm{Ran}(\delta_W) \subset \mathrm{Ker}(H_W - \epsilon_\mathrm{F}^W)$ with maximal rank N_p;

3. analyticity of the ground state: *the functions $W \mapsto \gamma_W$ and $W \mapsto \mathcal{E}^{\mathrm{rHF}}(W)$ are real analytic from $B_\eta(\mathcal{C}')$ to $\mathfrak{S}_{1,1}$ and $\mathbb{R}$ respectively. For all $W \in \mathcal{C}'$ and all $-\eta\|W\|_{\mathcal{C}'}^{-1} < \beta < \eta\|W\|_{\mathcal{C}'}^{-1}$,*

$$\gamma_{\beta W} = \gamma_0 + \sum_{k=1}^{+\infty} \beta^k \gamma_W^{(k)}, \quad \mathcal{E}^{\mathrm{rHF}}(\beta W) = \mathcal{E}^{\mathrm{rHF}}(0) + \sum_{k=1}^{+\infty} \beta^k \mathcal{E}_W^{(k)},$$

the series being normally convergent in $\mathfrak{S}_{1,1}$ and $\mathbb{R}$ respectively;

4. Rayleigh-Schrödinger expansions: *the coefficients $\gamma_W^{(k)}$ are given by (2.32), where the $A_W^{(k)}$'s are obtained recursively by solving the well-posed linear problem in $\mathcal{A}$*

$$\Theta(A_W^{(k)}) = -\frac{1}{2}B_W^{(k)}, \qquad (2.36)$$

where the $B_W^{(k)}$'s are defined by

$$\forall A \in \mathcal{A}, \quad \langle B_W^{(1)}, A\rangle = \int_{\mathbb{R}^3} \rho_{\gamma_1(A)} W, \tag{2.37}$$

and for all $k \geq 2$ and all $A \in \mathcal{A}$,

$$\begin{aligned}
\langle B_W^{(k)}, A\rangle = &\sum_{l=3}^{k+1} \sum_{\substack{\alpha \in (\mathbb{N}^*)^{l-1} \\ |\alpha|_1 = k,\, |\alpha|_\infty \leq k-1}} \sum_{i=1}^{l} \mathrm{Tr}\left(H_0 \gamma_l(\tau_{(i,l)}(A_W^{(\alpha_1)}, \cdots, A_W^{(\alpha_{l-1})}, A))\right) \\
&+ \sum_{\substack{3 \leq l+l' \leq k+1 \\ l \geq 1,\, l' \geq 1}} \sum_{\substack{\alpha \in (\mathbb{N}^*)^l,\, \alpha' \in (\mathbb{N}^*)^{l'-1} \\ |\alpha|_1 + |\alpha'|_1 = k,\, \max(|\alpha|_\infty, |\alpha'|_\infty) \leq k-1}} \sum_{i=1}^{l'} D\left(\rho_{\gamma^\alpha_{W,l}}, \rho_{\gamma_{l'}(\tau_{(i,l')}(A_W^{(\alpha'_1)}, \cdots, A_W^{(\alpha'_{l'-1})}, A))}\right) \\
&+ \sum_{l=2}^{k} \sum_{\substack{\alpha \in (\mathbb{N}^*)^{l-1} \\ |\alpha|_1 = k-1,\, |\alpha|_\infty \leq k-2}} \sum_{i=1}^{l} \int_{\mathbb{R}^3} \rho_{\gamma_l(\tau_{(i,l)}(A_W^{(\alpha_1)}, \cdots, A_W^{(\alpha_{l-1})}, A))} W;
\end{aligned} \tag{2.38}$$

where $\tau_{(i,j)}$ is the transposition swapping the i^{th} and j^{th} terms (by convention $\tau_{(i,i)}$ is the identity);

5. *first formulation of Wigner's $(2n+1)$-rule: for all $n \in \mathbb{N}$, and all $\epsilon \in \{0,1\}$,*

$$\begin{aligned}
\mathcal{E}_W^{(2n+\epsilon)} = &\sum_{2 \leq l \leq 2n+\epsilon} \sum_{\alpha \in (\mathbb{N}^*)^l \,|\, |\alpha|_1 = 2n+\epsilon,\, |\alpha|_\infty \leq n} \mathrm{Tr}\left(H_0 \gamma^\alpha_{W,l}\right) \\
&+ \frac{1}{2} \sum_{\substack{2 \leq l+l' \leq 2n+\epsilon \\ l,l' \geq 1}} \sum_{\substack{\alpha \in (\mathbb{N}^*)^l,\, \alpha' \in (\mathbb{N}^*)^{l'} \,|\, |\alpha|_1 + |\alpha'|_1 = 2n+\epsilon \\ \max(|\alpha|_\infty,\, |\alpha'|_\infty) \leq n}} D\left(\rho_{\gamma^\alpha_{W,l}}, \rho_{\gamma^{\alpha'}_{W,l'}}\right) \\
&+ \sum_{1 \leq l \leq 2n+\epsilon-1} \sum_{\alpha \in (\mathbb{N}^*)^l \,|\, |\alpha|_1 = 2n+\epsilon-1,\, |\alpha|_\infty \leq n} \int_{\mathbb{R}^3} \rho_{\gamma^\alpha_{W,l}} W;
\end{aligned} \tag{2.39}$$

6. *second formulation of Wigner's $(2n+1)$-rule: it holds*

$$0 \leq E^{\mathrm{rHF}}\left(\Gamma\left(\sum_{k=1}^{n} \beta^k A_W^{(k)}\right), W\right) - \mathcal{E}^{\mathrm{rHF}}(\beta W) = \mathcal{O}(|\beta|^{2n+2}). \tag{2.40}$$

Note that both formulations of Wigner's $(2n+1)$-rule state that an approximation of the energy $\mathcal{E}^{\mathrm{rHF}}(\beta W)$ up to order $(2n+1)$ in β, can be obtained from the $A_W^{(k)}$ for $1 \leq k \leq n$. They are yet different since the first formulation consists in computing all the coefficients $\mathcal{E}_W^{(k)}$ up to order $(2n+1)$, while the second formulation is based on the computation of the density matrix $\Gamma\left(\sum_{k=1}^{n} \beta^k A_W^{(k)}\right)$.

Remark 13. *Although we were not able to rigorously prove that assumptions (2.5), (2.8), (2.9) and (2.23) were actually satisfied for a specific molecular system, we strongly believe*

that this is the case for some atoms. Recall that the singlet-spin state rHF model is obtained from the spinless rHF model dealt with here by replacing N by $N/2$ (the number of electron pairs) and ρ_γ by $2\rho_\gamma$ (each state is occupied by one spin-up and one spin-down electron), so that all our results can be applied mutatis mutandis to the singlet-spin state rHF model. We have performed numerical simulations of a carbon atom within the singlet-spin state rHF model (see Chapter 4) and observed that for this system, the lowest two eigenvalues of H_0, corresponding to the 1s and 2s shells, are negative and non-degenerate, while the third lowest eigenvalue, corresponding to the 2p shell, is threefold degenerate. As the carbon atom contains six electrons, that is three electron pairs, the Fermi level coincides with the third lowest eigenvalue. Using the first statement of Proposition 3, we obtain that assumptions (2.8) is satisfied, hence that the ground state density matrix γ_0 is unique, yielding that, by symmetry, all the occupation numbers at the Fermi level are equal to $1/3$. Numerical simulations therefore suggest that assumptions (2.8), (2.9) and (2.23) are satisfied for the singlet-spin state rHF model of a carbon atom, while (2.5) is obviously satisfied since this system is electrically neutral.

Remark 14. *In order to illustrate what may happen when assumption (2.23) is not satisfied, we consider the toy model*

$$\mathcal{E}^{\mathrm{TM}}(w) = \inf\left\{E^{\mathrm{TM}}(\gamma, w),\ \gamma \in \mathcal{K}_2\right\}, \tag{2.41}$$

where

$$E^{\mathrm{TM}}(\gamma, w) = \mathrm{Tr}\left(H_0^{\mathrm{TM}}\gamma\right) + \frac{1}{2}\left(\mathrm{Tr}\ \left((\gamma - \gamma_0^{\mathrm{TM}})^2\right)\right)^2 + \mathrm{Tr}\left(\gamma w\right),$$

$$H_0^{\mathrm{TM}} = -2|e_1\rangle\langle e_1| - |e_2\rangle\langle e_2| - |e_3\rangle\langle e_3|, \quad \gamma_0^{\mathrm{TM}} = |e_1\rangle\langle e_1| + |e_2\rangle\langle e_2|,$$

e_1, e_2, e_3 being pairwise orthonormal vectors of $L^2(\mathbb{R}^3)$. For $w = 0$, the unique ground state of (2.41) is γ_0^{TM} and the mean-field Hamiltonian of the unperturbed system is H_0^{TM}. We are therefore in the degenerate case with $\epsilon_{\mathrm{F}}^0 = -1$ and $\delta_0^{\mathrm{TM}} = |e_2\rangle\langle e_2|$, and we have $N_{\mathrm{f}} = 1$, $1 = \mathrm{Rank}(\delta_0^{\mathrm{TM}}) < N_{\mathrm{p}} = 2$, $\mathrm{Ker}(1 - \delta_0^{\mathrm{TM}}) = \mathbb{R}e_2 \neq \{0\}$, so that condition (2.23) is not fulfilled. A simple calculation shows that for $w = |e_3\rangle\langle e_3|$, it holds

$$\mathcal{E}^{\mathrm{TM}}(\beta w) = \begin{cases} -3 - \frac{3}{8}|\beta|^{4/3} & \text{for } \beta < 0, \\ -3 & \text{for } \beta \geq 0. \end{cases}$$

Clearly, real-analytic perturbation theory cannot be applied.

Remark 15. *The block representation of $\gamma_W^{(1)}$, the first-order term of the perturbation expansion of the ground state density matrix, is given by*

$$\gamma_W^{(1)} = \begin{bmatrix} 0 & (A_{\mathrm{pf}}^{(1)})^*(1-\Lambda) & (A_{\mathrm{uf}}^{(1)})^* \\ (1-\Lambda)A_{\mathrm{pf}}^{(1)} & A_{\mathrm{pp}}^{(1)} & \Lambda(A_{\mathrm{up}}^{(1)})^* \\ A_{\mathrm{uf}}^{(1)} & A_{\mathrm{up}}^{(1)}\Lambda & 0 \end{bmatrix}, \tag{2.42}$$

where the above operators solve the following system

$$\Theta(A_{\rm uf}^{(1)}, A_{\rm up}^{(1)}, A_{\rm pf}^{(1)}, A_{\rm pp}^{(1)}) = -(W_{\rm uf}, W_{\rm up}\Lambda, (1-\Lambda)W_{\rm pf}, \frac{1}{2}W_{\rm pp}), \tag{2.43}$$

where W_{xy} is the xy-block of the operator "multiplication by W". We also have

$$\mathcal{E}_W^{(2)} = \mathrm{Tr}\left(H_0\gamma_{W,2}^{(1,1)}\right) + \frac{1}{2}D\left(\rho_{\gamma_{W,1}^{(1)}}, \rho_{\gamma_{W,1}^{(1)}}\right) + \int_{\mathbb{R}^3}\rho_{\gamma_{W,1}^{(1)}}W.$$

The second-order term $\gamma_W^{(2)}$ is also useful to compute nonlinear responses. The explicit formula is given in an appendix at the end of the chapter.

Remark 16. *In the degenerate case, there is no analogue of (2.12), that is no explicit closed recursion relation on the coefficients of the Rayleigh-Schrödinger expansion of the density.*

2.5 Extensions to other settings

Although all the results in the preceding sections are formulated for finite molecular systems in the whole space, in the all-electron rHF framework, some of them can be easily extended to other settings:

- all the results in Sections 2.3 and 2.4 can be extended to valence electron calculations with nonlocal pseudopotentials, as well as to regular nonlocal perturbations of the rHF model, that is to any perturbation modeled by an operator W such that $W(1-\Delta)$ is a bounded operator on $L^2(\mathbb{R}^3)$, the term $\int_{\mathbb{R}^3}\rho_\gamma W$ being then replaced with $\mathrm{Tr}\,(\gamma W)$;
- all the results in Section 2.3 can be extended to the rHF model for locally perturbed insulating or semiconducting crystals (see in particular [22], where the analogues of the operators $\mathcal{L}$ and $Q^{(k)}$ in Lemma 4 are introduced and analyzed); the extension to conducting crystals is a challenging task, see [34] for results on the particular case of the homogeneous electron gas;
- extending our results to the Kohn-Sham LDA model for finite molecular systems in the whole space is difficult as the ground state density decays exponentially to zero at infinity while the LDA exchange-correlation energy density is not twice differentiable at 0 (it behaves as the function $\mathbb{R}_+ \ni \rho \mapsto -\rho^{4/3} \in \mathbb{R}_-$). On the other hand, all the results in Sections 3 and 4 can be extended to the Kohn-Sham LDA model on a supercell with periodic boundary conditions as well as to the periodic Kohn-Sham LDA model for perfect crystals, as in this case, the ground state density is periodic and bounded away from zero (see e.g. [16, 17]). Let us emphasize however that in the LDA setting, it is not known whether the ground state density of the unperturbed problem is unique. We must therefore restrict ourselves to local perturbation theory in the vicinity of a local minimizer and make a coercivity assumption on the Hessian of the energy functional at the unperturbed local minimizer γ_0. In the supercell setting, the operator $\mathcal{L}$ was used in [29] to study the stability of crystals;

- the Hartree-Fock model consists in minimizing the energy functional

$$E^{\mathrm{HF}}(\gamma, W) := \mathrm{Tr}\left(-\frac{1}{2}\Delta\gamma\right) + \int_{\mathbb{R}^3} \rho_\gamma (V+W) + \frac{1}{2} D(\rho_\gamma, \rho_\gamma) - \frac{1}{2}\int_{\mathbb{R}^3}\int_{\mathbb{R}^3} \frac{|\gamma(x,y)|^2}{|x-y|}\, dx\, dy$$

over the set $\mathcal{P}_N$ of Slater determinants with finite kinetic energy. It turns out that all the local minimizers of $E^{\mathrm{HF}}(\gamma, W)$ on $\mathcal{K}_N$ are on $\mathcal{P}_N$ (Lieb's variational principle [56]). Consequently, an equivalent formulation of the Hartree-Fock model is

$$\mathcal{E}(W) := \inf\left\{E^{\mathrm{HF}}(\gamma, W),\ \gamma \in \mathcal{K}_N\right\}. \tag{2.44}$$

Uniqueness for problem (2.44) is an essentially open question (see however [42] for partial results). In order to apply perturbation theory, we therefore need a coercivity assumption on the Hessian at the minimizer γ_0, just as in the LDA setting. It is known that there are no unfilled shells in the Hartree-Fock theory [6], which implies that we are always in the non-degenerate case. The first three statements and the fifth statement of Theorem 5 can be transposed to the Hartree-Fock setting under the above mentioned coercivity assumption. On the other hand, there is no analogue of (2.12) for the Hartree-Fock model. A mathematical analysis of the perturbation theory for the molecular orbital formulation of the Hartree-Fock model was published in [21]. It is easily checked that our proof of Wigner's $(2n+1)$-rule also applies to the Hartree-Fock setting;

- the extension to some of our results to Stark potentials $W(x) = -E\cdot x$, where $E \in \mathbb{R}^3$ is a uniform electric field, will be dealt with in a future work [25].

2.6 Proofs

2.6.1 Proof of Lemma 2

Let γ_0 and γ_0' be two ground states of (2.4) for $W = 0$. By Theorem 1, $\gamma_0 - \gamma_0' = \sigma$, with $\sigma \in \mathcal{S}(L^2(\mathbb{R}^3))$, $\mathrm{Ran}(\sigma) \subset \mathrm{Ker}(H_0 - \epsilon_{\mathrm{F}}^0)$, $\mathrm{Tr}\,(\sigma) = 0$. Therefore,

$$\sigma = \sum_{i,j=1}^{N_{\mathrm{p}}} M_{ij} |\phi^0_{N_{\mathrm{f}}+i}\rangle\langle\phi^0_{N_{\mathrm{f}}+j}|$$

for some symmetric matrix $M \in \mathbb{R}_{\mathrm{S}}^{N_{\mathrm{p}}\times N_{\mathrm{p}}}$ such that $\mathrm{Tr}\,(M) = 0$. As, still by Theorem 1, γ_0 and γ_0' share the same density, the density of σ is identically equal to zero, that is

$$\forall x \in \mathbb{R}^3, \quad \sum_{i,j=1}^{N_{\mathrm{p}}} M_{ij}\phi^0_{N_{\mathrm{f}}+i}(x)\phi^0_{N_{\mathrm{f}}+j}(x) = 0.$$

If Assumption (2.9) is satisfied, then $M = 0$; therefore $\sigma = 0$, and uniqueness is proved.

2.6.2 Proof of Proposition 3

Let us first notice that as for all $1 \leq i \leq N_{\rm p}$, $\phi^0_{N_{\rm f}+i} \in D(H_0) = H^2(\mathbb{R}^3) \hookrightarrow C^0(\mathbb{R}^3)$, condition (2.9) is mathematically well-defined.

Case 1: Let $M \in \mathbb{R}^{N_{\rm p}\times N_{\rm p}}_{\rm S}$ be such that

$$\forall x \in \mathbb{R}^3, \quad \sum_{i,j=1}^{N_{\rm p}} M_{ij}\phi^0_{N_{\rm f}+i}(x)\phi^0_{N_{\rm f}+j}(x) = 0.$$

The matrix M being symmetric, there exists an orthogonal matrix $U \in O(N_{\rm p})$ such that $UMU^T = \mathrm{diag}(n_1, \cdots, n_{N_{\rm p}})$ with $n_1 \leq \cdots \leq n_{N_{\rm p}}$. Let $\widetilde{\phi}^0_{N_{\rm f}+i}(x) = \sum_{j=1}^{N_{\rm p}} U_{ij}\phi^0_{N_{\rm f}+j}(x)$. The functions $\widetilde{\phi}^0_{N_{\rm f}+i}$ form an orthonormal basis of $\mathrm{Ker}(H_0 - \epsilon^0_{\rm F})$ and it holds

$$\forall x \in \mathbb{R}^3, \quad \sum_{i=1}^{N_{\rm p}} n_i|\widetilde{\phi}^0_{N_{\rm f}+i}(x)|^2 = 0,$$

from which we deduce that $\sum_{i=1}^{N_{\rm p}} n_i = 0$. Consider first the case when $N_{\rm p} = 2$. If $M \neq 0$, then $n_2 = -n_1 = n > 0$, so that

$$\forall x \in \mathbb{R}^3, \quad |\widetilde{\phi}^0_{N_{\rm f}+1}(x)|^2 = |\widetilde{\phi}^0_{N_{\rm f}+2}(x)|^2.$$

In particular, the two eigenfunctions $\widetilde{\phi}^0_{N_{\rm f}+1}$ and $\widetilde{\phi}^0_{N_{\rm f}+2}$ have the same nodal surfaces (that is $(\widetilde{\phi}^0_{N_{\rm f}+1})^{-1}(0) = (\widetilde{\phi}^0_{N_{\rm f}+2})^{-1}(0)$). Consider now the case when $N_{\rm p} = 3$. If $M \neq 0$, then either $n_2 = 0$ and $\widetilde{\phi}^0_{N_{\rm f}+1}$ and $\widetilde{\phi}^0_{N_{\rm f}+3}$ have the same nodes, or $n_2 \neq 0$. Replacing M with $-M$, we can, without loss of generality assume that $n_1 < 0 < n_2 \leq n_3$, which leads to

$$\forall x \in \mathbb{R}^3, \quad |\widetilde{\phi}^0_{N_{\rm f}+1}(x)|^2 = \frac{|n_2|}{|n_1|}|\widetilde{\phi}^0_{N_{\rm f}+2}(x)|^2 + \frac{|n_3|}{|n_1|}|\widetilde{\phi}^0_{N_{\rm f}+3}(x)|^2.$$

We infer from the above equality that the nodal surfaces of $\widetilde{\phi}^0_{N_{\rm f}+1}(x)$ are included in those of $\widetilde{\phi}^0_{N_{\rm f}+2}(x)$. Let Ω be a connected component of the open set $\mathbb{R}^3 \setminus (\widetilde{\phi}^0_{N_{\rm f}+1})^{-1}(0)$, and let H^Ω_0 be the self-adjoint operator on $L^2(\Omega)$ with domain

$$D(H^\Omega_0) = \left\{u \in H^1_0(\Omega) \mid \Delta u \in L^2(\Omega)\right\}$$

defined by

$$\forall u \in D(H^\Omega_0), \quad H^\Omega_0 u = -\frac{1}{2}\Delta u + Vu + (\rho_0 \star |\cdot|^{-1})u.$$

As both $\psi_1 = \widetilde{\phi}^0_{N_{\rm f}+1}|_\Omega$ and $\psi_2 = \widetilde{\phi}^0_{N_{\rm f}+2}|_\Omega$ are in $D(H^\Omega_0)$ and satisfy $H^\Omega_0\psi_1 = \epsilon^0_{\rm F}\psi_1$, $H^\Omega_0\psi_2 = \epsilon^0_{\rm F}\psi_2$, $|\psi_1| > 0$ in Ω, we deduce from [69, Theorem XIII.44] that $\epsilon^0_{\rm F}$ is the non-degenerate ground state eigenvalue of H^Ω_0, so that there exists a real constant $C \in \mathbb{R}$ such that $\psi_2 = C\psi_1$. It follows from the unique continuation principle (see e.g. [69, Theorem XIII.57]) that $\widetilde{\phi}^0_{N_{\rm f}+2} = C\widetilde{\phi}^0_{N_{\rm f}+1}$ on $\mathbb{R}^3$, which contradicts the fact that $\widetilde{\phi}^0_{N_{\rm f}+1}$ and $\widetilde{\phi}^0_{N_{\rm f}+2}$ are orthogonal and non identically equal to zero. Thus, $M = 0$ and the proof of case 1 is complete.

Case 2. The degeneracy being assumed essential, $\epsilon_{\rm F}^0$ is $(2l+1)$-times degenerate for some integer $l \geq 1$, and there exists an orthonormal basis of associated eigenfunctions of the form

$$\forall 1 \leq i \leq N_{\rm p} = 2l+1, \quad \phi^0_{N_{\rm f}+i}(x) = R_l(r)\, \mathcal{Y}_l^{-l+i-1}(\theta,\varphi),$$

where (r,θ,φ) are the spherical coordinates of the point $x \in \mathbb{R}^3$, and where the functions $\mathcal{Y}_l^m$ are the spherical harmonics. In particular,

$$\sum_{i,j=1}^{2l+1} M_{ij} \phi^0_{N_{\rm f}+i}(x) \phi^0_{N_{\rm f}+j}(x) = R_l(r)^2 \sum_{i,j=1}^{2l+1} M_{ij}\, \mathcal{Y}_l^{-l+i-1}(\theta,\varphi)\, \mathcal{Y}_l^{-l+j-1}(\theta,\varphi).$$

We therefore have to prove that for any symmetric matrix $M \in \mathbb{R}_{\rm S}^{(2l+1)\times(2l+1)}$,

$$\left(\sum_{i,j=1}^{2l+1} M_{ij} \mathcal{Y}_l^{-l+i-1} \mathcal{Y}_l^{-l+j-1} = 0 \right) \; \Rightarrow \; M = 0.$$

Let $M \in \mathbb{R}_{\rm S}^{(2l+1)\times(2l+1)}$ a symmetric matrix such that

$$\sum_{i,j=1}^{2l+1} M_{ij} \mathcal{Y}_l^{-l+i-1} \mathcal{Y}_l^{-l+j-1} = 0$$

on the unit sphere $\mathbb{S}^2$. Using the relation

$$\mathcal{Y}_l^{m_1} \mathcal{Y}_l^{m_2} = \sum_{L=0}^{2l} \sqrt{\frac{(2l+1)^2(2L+1)}{4\pi}} \begin{pmatrix} l & l & L \\ & & \\ m_1 & m_2 & -(m_1+m_2) \end{pmatrix} \begin{pmatrix} l & l & L \\ & & \\ 0 & 0 & 0 \end{pmatrix} \mathcal{Y}_L^{m_1+m_2},$$

where the $\begin{pmatrix} l_1 & l_2 & l_3 \\ & & \\ m_1 & m_2 & m_3 \end{pmatrix}$ denote the Wigner 3-j symbols (see [15] for instance), and where, by convention, $\mathcal{Y}_L^m = 0$ whenever $|m| > L$, we obtain

$$\begin{aligned}
0 &= \frac{\sqrt{4\pi}}{2l+1} \sum_{i,j=1}^{2l+1} M_{ij} \mathcal{Y}_l^{-l+i-1} \mathcal{Y}_l^{-l+j-1} \\
&= \sum_{i,j=1}^{2l+1} M_{ij} \sum_{L=0}^{2l} \sqrt{2L+1} \begin{pmatrix} l & l & L \\ & & \\ -l+i-1 & -l+j-1 & 2l+2-i-j \end{pmatrix} \begin{pmatrix} l & l & L \\ & & \\ 0 & 0 & 0 \end{pmatrix} \mathcal{Y}_L^{i+j-2l-2} \\
&= \sum_{m=-2l}^{2l} \sum_{L=0}^{2l} \sqrt{2L+1} \begin{pmatrix} l & l & L \\ & & \\ 0 & 0 & 0 \end{pmatrix} \left[\sum_{\substack{1 \leq i,j \leq 2l+1 \\ i+j-2l-2=m}} \begin{pmatrix} l & l & L \\ & & \\ -l+i-1 & -l+j-1 & -m \end{pmatrix} M_{ij} \right] \mathcal{Y}_L^m.
\end{aligned}$$

Using the fact that the Wigner 3-j symbol $\begin{pmatrix} l & l & L \\ m_1 & m_2 & -(m_1+m_2) \end{pmatrix}$ is equal to zero unless

$$|m_1| \leq l, \quad |m_2| \leq l, \quad |m_1+m_2| \leq L, \quad 0 \leq L \leq 2l, \quad \text{and} \quad L \in 2\mathbb{N} \text{ if } m_1 = m_2 = 0,$$

we obtain that for all $L \in \{0, 2, \cdots, 2l\}$ and all $-L \leq m \leq L$,

$$\sum_{\substack{1 \leq i,j \leq 2l+1 \\ i+j-2l-2=m}} \begin{pmatrix} l & l & L \\ -l+i-1 & -l+j-1 & -m \end{pmatrix} M_{ij} = 0. \tag{2.45}$$

For $m = -2l$ and $L = 2l$, the above expression reduces to

$$\begin{pmatrix} l & l & 2l \\ -l & -l & 2l \end{pmatrix} M_{11} = 0, \qquad \text{where} \qquad \begin{pmatrix} l & l & 2l \\ -l & -l & 2l \end{pmatrix} = \frac{1}{\sqrt{4l+1}}.$$

Hence $M_{11} = 0$. More generally, for each integer value of m in the range $[-2l, 2l]$, equation (2.45) gives rise to a linear system of $n_{m,l}$ equations (obtained for the various even values of L in the range $[|m|, 2l]$) with $n_{m,l}$ unknowns (the $M_{i,j}$'s satisfying $i \leq j$ - recall that the matrix M is symmetric - and $i + j = 2l + 2 + m$). Using the symmetry property

$$\begin{pmatrix} l & l & L \\ -l+i-1 & -l+j-1 & -m \end{pmatrix} = \begin{pmatrix} l & l & L \\ -l+j-1 & -l+i-1 & -m \end{pmatrix}$$

and the orthogonality relation stating that for all $-2l \leq m \leq 2l$, and all $|m| \leq L, L' \leq 2l$,

$$\sum_{\substack{1 \leq i,j \leq 2l+1 \\ i+j-2l-2=m}} \begin{pmatrix} l & l & L \\ -l+i-1 & -l+j-1 & -m \end{pmatrix} \begin{pmatrix} l & l & L' \\ -l+i-1 & -l+j-1 & -m \end{pmatrix} = \frac{\delta_{LL'}}{(2L+1)},$$

it is easy to see that this linear system is free, and that the corresponding entries of M are therefore equal to 0. Hence, the matrix M is identically equal to zero, which completes the proof.

2.6.3 Proof of Lemma 4

As $\mathscr{C}$ is a compact subset of the resolvent set of H_0 and as the domain of H_0 is $H^2(\mathbb{R}^3)$, there exists $C_0 \in \mathbb{R}_+$ such that

$$\max_{z \in \mathscr{C}} (\|(z - H_0)^{-1}\|, \|(1-\Delta)(z-H_0)^{-1}\|, \|(z-H_0)(1-\Delta)^{-1}\|) \leq C_0.$$

It follows from the Kato-Seiler-Simon inequality [76] that for all $v \in \mathcal{C}'$,

$$\|v(z-H_0)^{-1}\| \leq C_0 \|v(1-\Delta)^{-1}\| \leq C_0 \|v(1-\Delta)^{-1}\|_{\mathfrak{S}_6} \leq C\|v\|_{L^6} \leq \alpha \|v\|_{\mathcal{C}'},$$

for constants $\alpha, C \in \mathbb{R}_+$ independent of v. The k-linear map $Q^{(k)}$ is therefore well-defined and continuous from $(\mathcal{C}')^k$ to the space of bounded operators on $L^2(\mathbb{R}^3)$. Denoting by $\gamma_0^\perp = 1 - \gamma_0$, we have

$$Q^{(k)}(v_1, \cdots, v_k) = \sum_{(P_j)_{0\leq j\leq k} \in \left\{\gamma_0, \gamma_0^\perp\right\}^{k+1}} \frac{1}{2i\pi} \oint_{\mathscr{C}} (z - H_0)^{-1} P_0 \prod_{j=1}^{k} \left(v_j (z - H_0)^{-1} P_j\right) \, dz.$$

In the above sum, the term with all the P_j's equal to $\gamma_0^\perp$ is equal to zero as a consequence of Cauchy's residue formula. In all the remaining terms, one of the P_j's is equal to the rank-N operator γ_0. The operators $(z - H_0)^{-1}$ and $v_j(z - H_0)^{-1}$ being bounded, $Q^{(k)}(v_1, \cdots, v_k)$ is finite-rank, hence trace-class, and it holds

$$\|Q^{(k)}(v_1, \cdots, v_k)\|_{\mathfrak{S}_1} \leq \frac{|\mathscr{C}|}{2\pi} N C_0 \alpha^k \|v_1\|_{\mathcal{C}'} \cdots \|v_k\|_{\mathcal{C}'}.$$

Likewise, the operator

$$|\nabla| Q^{(k)}(v_1, \cdots, v_k) |\nabla|$$
$$= \sum_{(P_j) \in \left\{\gamma_0, \gamma_0^\perp\right\}^{k+1}} \frac{1}{2i\pi} \oint_{\mathscr{C}} |\nabla| (z - H_0)^{-1/2} P_0 \prod_{j=1}^{k} \Big((z - H_0)^{-1/2} v_j (z - H_0)^{-1/2} P_j \Big) \, (z - H_0)^{-1/2} |\nabla| \, dz$$

is finite rank and

$$\| \, |\nabla| Q^{(k)}(v_1, \cdots, v_k) |\nabla| \, \|_{\mathfrak{S}_1} \leq C \alpha^k \|v_1\|_{\mathcal{C}'} \cdots \|v_k\|_{\mathcal{C}'},$$

for some constant C independent of $v_1, \cdots, v_k$. Therefore $Q^{(k)}$ is a continuous linear map from $(\mathcal{C}')^k$ to $\mathfrak{S}_{1,1}$ and the bound (2.10) holds true. It then follows from Cauchy's residue formula and the cyclicity of the trace that, for $k \geq 1$,

$$\begin{aligned}
\mathrm{Tr}\left(Q^{(k)}(v_1, \cdots, v_k)\right) &= \mathrm{Tr}\left(\frac{1}{2i\pi} \oint_{\mathscr{C}} (z - H_0)^{-1} \prod_{j=1}^{k} \left(v_j (z - H_0)^{-1}\right) \, dz \right) \\
&= \sum_{(P_j) \in \left\{\gamma_0, \gamma_0^\perp\right\}^{k+1}} \mathrm{Tr}\left(\frac{1}{2i\pi} \oint_{\mathscr{C}} (z - H_0)^{-1} P_0 \prod_{j=1}^{k} \left(v_j (z - H_0)^{-1} P_j\right) \, dz \right) \\
&= \sum_{j=1}^{k} \sum_{(P_l) \in \left\{\gamma_0, \gamma_0^\perp\right\}^{k}} \mathrm{Tr}\left(\frac{1}{2i\pi} \oint_{\mathscr{C}} \prod_{l=1}^{k-1} \left(v_{l+j \bmod(k)} (z - H_0)^{-1} P_l\right) v_j (z - H_0)^{-2} \gamma_0 \, dz \right) = 0.
\end{aligned}$$

Let $\rho \in \mathcal{C}$ and $Q := Q^{(1)}(\rho \star |\cdot|^{-1})$. Proceeding as above, we obtain that for all $\phi \in C_{\mathrm{c}}^\infty(\mathbb{R}^3)$,

$$\begin{aligned}
\left| \int_{\mathbb{R}^3} \rho_Q \phi \right| &= |\mathrm{Tr}\,(Q\phi)| = \left| \mathrm{Tr}\left(\frac{1}{2i\pi} \oint_{\mathscr{C}} (z - H_0)^{-1} (\rho \star |\cdot|^{-1}) (z - H_0)^{-1} \phi \, dz \right) \right| \\
&\leq C \|\rho\|_{\mathcal{C}} \|\phi\|_{\mathcal{C}'},
\end{aligned}$$

for a constant $C \in \mathbb{R}_+$ independent of ρ and ϕ. Therefore, ρ_Q is in $\mathcal{C}$ and $\|\rho_Q\|_{\mathcal{C}} \leq C\|\rho\|_{\mathcal{C}}$. This proves that $\mathcal{L}$ is a bounded operator on $\mathcal{C}$. In addition, for all ρ_1, ρ_2 in $\mathcal{C}$,

$$(\mathcal{L}\rho_1, \rho_2)_{\mathcal{C}} = -\mathrm{Tr}\left(\frac{1}{2i\pi}\oint_{\mathscr{C}} (z - H_0)^{-1}(\rho_1 \star |\cdot|^{-1})(z - H_0)^{-1}(\rho_2 \star |\cdot|^{-1})\, dz\right) = (\rho_1, \mathcal{L}\rho_2)_{\mathcal{C}},$$

where we have used again the cyclicity of the trace. Thus, $\mathcal{L}$ is self-adjoint. Lastly, for all $\rho \in \mathcal{C}$,

$$(\mathcal{L}\rho, \rho)_{\mathcal{C}} = \sum_{i=1}^{N} \langle \gamma_0^{\perp}((\rho \star |\cdot|^{-1})\phi_i^0) | (H_0^{\perp} - \epsilon_i)^{-1} | \gamma_0^{\perp}((\rho \star |\cdot|^{-1})\phi_i^0)\rangle \geq 0,$$

where $H_0^{\perp}$ is the self-adjoint operator on $\mathrm{Ran}(\gamma_0^{\perp}) = \mathrm{Ker}(\gamma_0)$ defined by $\forall v \in \mathrm{Ran}(\gamma_0^{\perp})$, $H_0^{\perp} v = H_0 v$.

2.6.4 Stability of the spectrum of the mean-field Hamiltonian

We assume here that we are

- either in the non-degenerate case ($\epsilon_N < 0$ and $\epsilon_N < \epsilon_{N+1}$), in which case we set $\epsilon_{\mathrm{F}}^0 = \frac{\epsilon_N + \epsilon_{N+1}}{2}$;
- or in the degenerate case ($\epsilon_N = \epsilon_{N+1} = \epsilon_{\mathrm{F}}^0 < 0$).

We recall that $N_{\mathrm{f}} = \mathrm{Rank}(\mathbb{1}_{(-\infty, \epsilon_{\mathrm{F}}^0)}(H_0))$, $N_{\mathrm{p}} = \mathrm{Rank}(\mathbb{1}_{\{\epsilon_{\mathrm{F}}^0\}}(H_0))$ and $N_{\mathrm{o}} = N_{\mathrm{f}} + N_{\mathrm{p}}$. We also have $g_- = \epsilon_{\mathrm{F}}^0 - \epsilon_{N_{\mathrm{f}}}$ and $g_+ = \epsilon_{N_{\mathrm{f}}+N_{\mathrm{p}}+1} - \epsilon_{\mathrm{F}}^0$. By definition $g_- > 0$ and $g_+ > 0$ since $\epsilon_{\mathrm{F}}^0 < 0$.

Lemma 17. *Let*

$$\alpha_1 = \epsilon_1 - 1,\ \alpha_2 = \epsilon_{\mathrm{F}}^0 - \frac{3g_-}{4},\ \alpha_3 = \epsilon_{\mathrm{F}}^0 - \frac{g_-}{4},\ \alpha_4 = \epsilon_{\mathrm{F}}^0 + \frac{g_+}{4},\ \alpha_5 = \epsilon_{\mathrm{F}}^0 + \frac{3g_+}{4}.$$

There exists $\eta > 0$ such that for all $v \in B_\eta(\mathcal{C}')$,

$$\mathrm{Rank}(\mathbb{1}_{(-\infty,\alpha_1]}(H_0 + v)) = 0,\ \mathrm{Rank}(\mathbb{1}_{(\alpha_1,\alpha_2)}(H_0 + v)) = N_{\mathrm{f}},\ \mathrm{Rank}(\mathbb{1}_{[\alpha_2,\alpha_3]}(H_0 + v)) = 0,$$
$$\mathrm{Rank}(\mathbb{1}_{(\alpha_3,\alpha_4]}(H_0 + v)) = N_{\mathrm{p}},\ \mathrm{Rank}(\mathbb{1}_{(\alpha_4,\alpha_5]}(H_0 + v)) = 0.$$

Proof. Let $z \in \{\alpha_1, \alpha_2, \alpha_3, \alpha_4, \alpha_5\}$. As $z \notin \sigma(H_0)$, we have

$$z - (H_0 + v) = \left(1 + v(1 - \Delta)^{-1}(1 - \Delta)(z - H_0)^{-1}\right)\ (z - H_0).$$

Besides, as $D(H_0) = H^2(\mathbb{R}^3)$, there exists a constant $C \in \mathbb{R}_+$ independent of the choice of $z \in \{\alpha_1, \alpha_2, \alpha_3, \alpha_4, \alpha_5\}$, such that

$$\|(1 - \Delta)(z - H_0)^{-1}\| \leq C.$$

In addition, there exists a constant $C' \in \mathbb{R}_+$ such that for all $v \in \mathcal{C}'$,

$$\|v(1 - \Delta)^{-1}\| \leq \|v(1 - \Delta)^{-1}\|_{\mathfrak{S}_6} \leq C'\|v\|_{\mathcal{C}'}.$$

Let $\eta = (CC')^{-1}$. We obtain that for all $v \in B_\eta(\mathcal{C}')$,

$$\|v(1-\Delta)^{-1}(1-\Delta)(z-H_0)^{-1}\| < 1,$$

so that $z-(H_0+v)$ is invertible. Therefore, for all $v \in B_\eta(\mathcal{C}')$, none of the real numbers $\alpha_1, \alpha_2, \alpha_3, \alpha_4, \alpha_5$ are in $\sigma(H_0+v)$. It also follows from the above arguments that for all $v \in \mathcal{C}'$, the multiplication by v is a H_0-bounded operator on $L^2(\mathbb{R}^3)$. Using Kato's perturbation theory, we deduce from a simple continuity argument that the ranks of the spectral projectors

$$\mathbb{1}_{(-\infty,\alpha_1]}(H_0+v),\ \mathbb{1}_{(\alpha_1,\alpha_2)}(H_0+v),\ \mathbb{1}_{[\alpha_2,\alpha_3]}(H_0+v),\ \mathbb{1}_{(\alpha_3,\alpha_4]}(H_0+v),\ \text{and } \mathbb{1}_{(\alpha_4,\alpha_5]}(H_0+v)$$

are constant for $v \in B_\eta(\mathcal{C}')$, and therefore equal to their values for $v=0$, namely 0, $N_{\rm f}$, 0, $N_{\rm p}$ and 0 respectively. □

2.6.5 Proof of Theorem 5

Step 1: proof of statement 1.

Let us introduce the relaxed constrained problem

$$\mathcal{E}^{\rm rHF}_{\leq N}(W) = \inf\left\{E^{\rm rHF}(\gamma,W),\ \gamma \in \mathcal{K}_{\leq N}\right\}, \tag{2.46}$$

where

$$\mathcal{K}_{\leq N} = \left\{\gamma \in \mathcal{S}(L^2(\mathbb{R}^3)) \mid 0 \leq \gamma \leq 1,\ \mathrm{Tr}\,(\gamma) \leq N,\ \mathrm{Tr}\,(-\Delta\gamma) < \infty\right\}.$$

As $\epsilon^0_{\rm F} < 0$, γ_0 is the unique minimizer of (2.46) for $W=0$, and as $\mathcal{K}_{\leq N}$ is convex, the corresponding optimality condition reads

$$\forall \gamma \in \mathcal{K}_{\leq N}, \quad \mathrm{Tr}\,(H_0(\gamma-\gamma_0)) \geq 0. \tag{2.47}$$

Let $W \in \mathcal{C}'$, and $(\gamma'_k)_{k\in\mathbb{N}^*}$ a minimizing sequence for (2.46) for which

$$\forall k \geq 1, \quad E^{\rm rHF}(\gamma'_k,W) \leq \mathcal{E}^{\rm rHF}_{\leq N}(W) + \frac{1}{k}. \tag{2.48}$$

Set $\rho'_k = \rho_{\gamma'_k}$. We obtain on the one hand, using (2.47),

$$\begin{aligned}
\mathcal{E}^{\rm rHF}_{\leq N}(W) &\geq E^{\rm rHF}(\gamma'_k,W) - \frac{1}{k} \\
&= E^{\rm rHF}(\gamma'_k,0) + \int_{\mathbb{R}^3}\rho'_k W - \frac{1}{k} \\
&= \mathcal{E}^{\rm rHF}_{\leq N}(0) + \mathrm{Tr}\,(H_0(\gamma'_k-\gamma_0)) + \frac{1}{2}D(\rho'_k-\rho_0,\rho'_k-\rho_0) + \int_{\mathbb{R}^3}\rho'_k W - \frac{1}{k} \\
&\geq \mathcal{E}^{\rm rHF}_{\leq N}(0) + \frac{1}{2}D(\rho'_k-\rho_0,\rho'_k-\rho_0) + \int_{\mathbb{R}^3}\rho'_k W - \frac{1}{k},
\end{aligned}$$

and on the other hand

$$\mathcal{E}^{\rm rHF}_{\leq N}(W) \leq E^{\rm rHF}(\gamma_0,W) = \mathcal{E}^{\rm rHF}_{\leq N}(0) + \int_{\mathbb{R}^3}\rho_0 W.$$

Therefore,

$$\frac{1}{2}D(\rho'_k-\rho_0,\rho'_k-\rho_0)\leq\int_{\mathbb{R}^3}(\rho_0-\rho'_k)W+\frac{1}{k},$$

from which we get

$$\frac{1}{2}\|\rho'_k-\rho_0\|_{\mathcal{C}}^2\leq\|W\|_{\mathcal{C}'}\|\rho'_k-\rho_0\|_{\mathcal{C}}+\frac{1}{k},$$

and finally

$$\|\rho'_k-\rho_0\|_{\mathcal{C}}\leq 2\|W\|_{\mathcal{C}'}+\left(2k^{-1}\right)^{1/2}. \tag{2.49}$$

Then, using Cauchy-Schwarz, Hardy and Hoffmann-Ostenhof [52] inequalities, we obtain

$$\begin{aligned}
\mathcal{E}^{\mathrm{rHF}}_{\leq N}(0) &= \mathcal{E}^{\mathrm{rHF}}(0)=E^{\mathrm{rHF}}(\gamma_0,0)=E^{\mathrm{rHF}}(\gamma_0,W)-\int_{\mathbb{R}^3}\rho_0 W\\
&\geq \mathcal{E}^{\mathrm{rHF}}_{\leq N}(W)-\int_{\mathbb{R}^3}\rho_0 W\geq E^{\mathrm{rHF}}(\gamma'_k,W)-\int_{\mathbb{R}^3}\rho_0 W-\frac{1}{k}\\
&= \frac{1}{2}\mathrm{Tr}\,(-\Delta\gamma'_k)+\int_{\mathbb{R}^3}V\rho'_k+\frac{1}{2}D(\rho'_k,\rho'_k)+\int_{\mathbb{R}^3}\rho'_k W-\int_{\mathbb{R}^3}\rho_0 W-\frac{1}{k}\\
&\geq \frac{1}{2}\mathrm{Tr}\,(-\Delta\gamma'_k)-2ZN^{\frac{1}{2}}(\mathrm{Tr}\,(-\Delta\gamma'_k))^{1/2}+\frac{1}{2}\|\rho'_k\|_{\mathcal{C}}^2-\|\rho'_k\|_{\mathcal{C}}\|W\|_{\mathcal{C}'}-\|\rho_0\|_{\mathcal{C}}\|W\|_{\mathcal{C}'}-\frac{1}{k}\\
&\geq \frac{1}{2}((\mathrm{Tr}\,(-\Delta\gamma'_k))^{1/2}-2ZN^{\frac{1}{2}})^2+\frac{1}{2}(\|\rho'_k\|_{\mathcal{C}}-\|W\|_{\mathcal{C}'})^2-2Z^2N-\frac{1}{2}\|\rho_0\|_{\mathcal{C}}^2-\|W\|_{\mathcal{C}'}^2-\frac{1}{k}\\
&\geq \frac{1}{2}((\mathrm{Tr}\,(-\Delta\gamma'_k))^{1/2}-2ZN^{\frac{1}{2}})^2-2Z^2N-\frac{1}{2}\|\rho_0\|_{\mathcal{C}}^2-\|W\|_{\mathcal{C}'}^2-\frac{1}{k},
\end{aligned}$$

from which we infer that

$$\mathrm{Tr}\,(-\Delta\gamma'_k)\leq C_0(1+\|W\|_{\mathcal{C}'}^2),$$

for some constant $C_0\in\mathbb{R}_+$ independent of W and k. This estimate, together with (2.49) and the fact that $\|\gamma'_k\|_{\mathfrak{S}_1}=\mathrm{Tr}\,(\gamma'_k)\leq N$, shows that the sequences $(\gamma'_k)_{k\in\mathbb{N}^*}$ and $(\rho'_k)_{k\in\mathbb{N}^*}$ are bounded in $\mathfrak{S}_{1,1}$ and $\mathcal{C}$ respectively. We can therefore extract from $(\gamma'_k)_{k\in\mathbb{N}^*}$ a subsequence $(\gamma'_{k_j})_{j\in\mathbb{N}^*}$ such that $(\gamma'_{k_j})_{j\in\mathbb{N}}$ converges to γ_W for the weak-$*$ topology of $\mathfrak{S}_{1,1}$, and $(\rho'_{k_j})_{j\in\mathbb{N}}$ converges to $\rho_W:=\rho_{\gamma_W}$ weakly in $\mathcal{C}$ and strongly in $L^p_{\mathrm{loc}}(\mathbb{R}^3)$ for all $1\leq p<3$. This implies that

$$\gamma_W\in\mathcal{K}_{\leq N}\quad\text{and}\quad E^{\mathrm{rHF}}(\gamma_W,W)\leq\liminf_{j\to\infty}E^{\mathrm{rHF}}(\gamma'_{k_j},W)=\mathcal{E}^{\mathrm{rHF}}_{\leq N}(W).$$

Thus γ_W is a minimizer of (2.46). In addition, as the rHF model is strictly convex in the density, all the minimizers of (2.46) have the same density ρ_W, and, passing in the limit in (2.49), we obtain that ρ_W satisfies

$$\|\rho_W-\rho_0\|_{\mathcal{C}}\leq 2\|W\|_{\mathcal{C}'}.$$

Denoting by

$$v_W=W+(\rho_W-\rho_0)\star|\cdot|^{-1}, \tag{2.50}$$

we have

$$H_W=-\frac{1}{2}\Delta+V+W+\rho_W\star|\cdot|^{-1}=H_0+v_W, \tag{2.51}$$

with

$$\|v_W\|_{\mathcal{C}'} \leq \|W\|_{\mathcal{C}'} + \|(\rho_W - \rho_0) \star |\cdot|^{-1}\|_{\mathcal{C}'} \leq 3\|W\|_{\mathcal{C}'}. \tag{2.52}$$

By Lemma 17, for all $W \in B_{\eta/3}(\mathcal{C}')$, we have

$$\mathrm{Rank}(\mathbb{1}_{(-\infty,\epsilon_{\mathrm{F}}^0 - g_-/2]}(H_W)) = N \quad \text{and} \quad \mathrm{Rank}(\mathbb{1}_{(\epsilon_{\mathrm{F}}^0 - g_-/2, \epsilon_{\mathrm{F}}^0 + g_-/2]}(H_W)) = 0.$$

In particular, H_W has a least N negative eigenvalues, from which we infer that $\mathrm{Tr}\,(\gamma_W) = N$. Therefore, γ_W is a minimizer of (2.4). In addition, $\gamma_W = \mathbb{1}_{(-\infty,\epsilon_{\mathrm{F}}^0]}(H_W)$ and it holds

$$\gamma_W = \frac{1}{2i\pi} \oint_{\mathscr{C}} (z - H_W)^{-1}\, dz. \tag{2.53}$$

Step 2: proof of statement 2.

It follows from (2.50), (2.51) and (2.53) that

$$\forall W \in B_{\eta/3}(\mathcal{C}'), \quad \mathcal{X}(v_W) = W,$$

where $\mathcal{X}$ is the mapping from $B_{\eta/3}(\mathcal{C}')$ to $\mathcal{C}'$ defined by

$$\mathcal{X}(v) = v - \rho_{\frac{1}{2i\pi}\oint_{\mathscr{C}}((z-H_0-v)^{-1} - (z-H_0)^{-1})\,dz} \star |\cdot|^{-1}.$$

The mapping $\mathcal{X}$ is real analytic. Besides, denoting by v_{c} the Coulomb operator associating to each density $\rho \in \mathcal{C}$ the electrostatic potential $v_{\mathrm{c}}(\rho) = \rho \star |\cdot|^{-1} \in \mathcal{C}'$, we have

$$\mathcal{X}'(0) = v_{\mathrm{c}}(1 + \mathcal{L})v_{\mathrm{c}}^{-1}.$$

It follows from the second statement of Lemma 4 and from the fact that $v_{\mathrm{c}} : \mathcal{C} \to \mathcal{C}'$ is a bijective isometry that $\mathcal{X}'(0)$ is bijective. Applying the real analytic implicit function theorem, we obtain that the mapping $W \mapsto v_W$ is real analytic from some ball $B_{\eta'}(\mathcal{C}')$ (for some $\eta' > 0$) to $\mathcal{C}'$. By composition of real analytic functions, the functions

$$\gamma_W = \frac{1}{2i\pi} \oint_{\mathscr{C}} (z - H_0 - v_W)^{-1}\, dz,\ \rho_W = \rho_0 + v_{\mathrm{c}}^{-1}(v_W - W) \text{ and } \mathcal{E}^{\mathrm{rHF}}(W) = E^{\mathrm{rHF}}(\gamma_W, W)$$

are real analytic from $B_{\eta'}(\mathcal{C}')$ to $\mathfrak{S}_{11}$, $\mathcal{C}$ and $\mathbb{R}$ respectively.

Step 3: proof of statements 3 and 4.

Let $W \in B_{\eta'}(\mathcal{C}')$. It follows from the above result that the functions $\beta \mapsto \gamma_{\beta W}$, $\beta \mapsto \rho_{\beta W}$, and $\beta \mapsto \mathcal{E}^{\mathrm{rHF}}(\beta W)$ are real analytic in the vicinity of 0, so that, for $|\beta|$ small enough,

$$\gamma_{\beta W} = \gamma_0 + \sum_{k=1}^{+\infty} \beta^k \gamma_W^{(k)}, \quad \rho_{\beta W} = \rho_0 + \sum_{k=1}^{+\infty} \beta^k \rho_W^{(k)}, \quad \mathcal{E}^{\mathrm{rHF}}(\beta W) = \mathcal{E}^{\mathrm{rHF}}(0) + \sum_{k=1}^{+\infty} \beta^k \mathcal{E}_W^{(k)},$$

the series being normally convergent in $\mathfrak{S}_{11}$, $\mathcal{C}$ and $\mathbb{R}$ respectively. The Dyson expansion of (2.11) gives

$$\gamma_{\beta W} \quad = \quad \gamma_0 + \sum_{k=1}^{+\infty} Q^{(k)}\left(v_{\beta W}, \cdots, v_{\beta W}\right).$$

As

$$v_{\beta W} = \beta W + \sum_{k=1}^{+\infty} \beta^k (\rho_W^{(k)} \star |\cdot|^{-1}) = \sum_{k=1}^{+\infty} \beta^k W^{(k)},$$

where we recall that $W^{(1)} = W + \rho_W^{(1)} \star |\cdot|^{-1}$ and $W^{(k)} = \rho_W^{(k)} \star |\cdot|^{-1}$, we obtain

$$\gamma_{\beta W} = \gamma_0 + \sum_{k=1}^{+\infty} Q^{(k)} \left(\sum_{j=1}^{+\infty} \beta^j W^{(j)}, \cdots, \sum_{j=1}^{+\infty} \beta^j W^{(j)} \right),$$

from which we deduce (2.14). Taking the densities of both sides of (2.14), we get

$$\rho_W^{(k)} = -\mathcal{L}(\rho_W^{(k)}) + \widetilde{\rho}_W^{(k)}.$$

This proves (2.12).

2.6.6 Proof of Lemma 6 and of (2.18)

The proof of Lemma 6 is similar to the proof of Lemma 1 in [21]. We only sketch it here for brevity. We denote by $\mathcal{V} := (H^1(\mathbb{R}^3))^N$, by $\Phi^0 = (\phi_1^0, \cdots, \phi_N^0)^T \in \mathcal{V}$ and by $\mathscr{H}$ the bounded linear operator from $\mathcal{V}$ to $\mathcal{V}' \equiv (H^{-1}(\mathbb{R}^3))^N$ defined by

$$\forall \Psi \in \mathcal{V}, \quad (\mathscr{H}\Psi)_i = (H_0 - \epsilon_i)\psi_i + \sum_{j=1}^{N} K_{ij}^0 \psi_j.$$

We then decompose $\mathcal{V}$ as

$$\mathcal{V} = \mathbb{S}\Phi^0 + \mathbb{A}\Phi^0 + \Phi_\perp^0 = \mathbb{D}\Phi^0 + \mathbb{S}^0\Phi^0 + \mathbb{A}\Phi^0 + \Phi_\perp^0,$$

where $\mathbb{D}$, $\mathbb{A}$, $\mathbb{S}$, and $\mathbb{S}^0$ denote the vector spaces of $N \times N$ real-valued matrices which are respectively diagonal, antisymmetric, symmetric, and symmetric with zero entries on the diagonal, and where

$$\Phi_\perp^0 = \left\{ \Phi = (\phi_i)_{1 \le i \le N} \in \mathcal{V} \mid \forall 1 \le i, j \le N,\ (\phi_i, \phi_j^0)_{L^2} = 0 \right\}.$$

Likewise, it holds

$$\mathcal{V}' = \mathbb{S}\Phi^0 + \mathbb{A}\Phi^0 + \Phi_{\perp\!\!\perp}^0 \quad \text{with} \quad \Phi_{\perp\!\!\perp}^0 = \left\{ g = (g_i)_{1 \le i \le N} \in \mathcal{V}' \mid \forall 1 \le i, j \le N,\ \langle g_i, \phi_j^0 \rangle = 0 \right\}$$

and it is easily checked that

$$\left\{ g \in \mathcal{V}' \mid \forall \chi \in \Phi_\perp^0,\ \langle g, \chi \rangle = 0 \right\} = \mathbb{S}\Phi^0 + \mathbb{A}\Phi^0. \tag{2.54}$$

Denoting by $F = (f_1, \cdots, f_N)^T \in \mathcal{V}'$ and by $\alpha \in \mathbb{D}$ the $N \times N$ diagonal matrix with entries $\alpha_1, \cdots, \alpha_N$, we have to show that there exists a unique pair $(\Psi, \eta) \in \mathcal{V} \times \mathbb{D}$ such that

$$\begin{cases} \mathscr{H}\Psi = F + \eta\Phi^0, \\ \Psi - \alpha\Phi^0 \in \mathbb{S}^0\Phi^0 + \mathbb{A}\Phi^0 + \Phi_\perp^0. \end{cases} \tag{2.55}$$

For this purpose, we first introduce the matrix $S \in \mathbb{S}$ defined by

$$\forall 1 \le i \le N,\ S_{ii} = \alpha_i \quad \text{and} \quad \forall 1 \le i \ne j \le N,\ S_{ij} = \frac{\langle f_j, \phi_i^0 \rangle - \langle f_i, \phi_j^0 \rangle}{\epsilon_j - \epsilon_i},$$

and observe that $\widetilde{F} := F - \mathscr{H}(S\Phi^0) \in \mathbb{S}\Phi^0 + \Phi^0_{\perp\!\!\!\perp}$. Next, using the fact that $\epsilon_1 < \cdots < \epsilon_N < \epsilon_{\rm F}^0$ and the positivity of the operator K^0, namely

$$\forall \Psi = (\psi_i)_{1\le i\le N} \in \mathcal{V}, \quad \sum_{i,j=1}^N \langle K_{ij}^0 \psi_j, \psi_i \rangle = 2\, D\left(\sum_{i=1}^N \phi_i^0 \psi_i, \sum_{i=1}^N \phi_i^0 \psi_i \right) \ge 0,$$

we can see that the operator $\mathscr{H}$ is coercive on $\Phi^0_\perp$. Therefore, by Lax-Milgram lemma and (2.54), there exists a unique $\widetilde{\Psi} \in \Phi^0_\perp$ such that $\mathscr{H}\widetilde{\Psi} - \widetilde{F} \in \mathbb{S}\Phi^0 + \mathbb{A}\Phi^0$. As $\widetilde{F} \in \mathbb{S}\Phi^0 + \Phi^0_{\perp\!\!\!\perp}$ and

$$\forall 1 \le i,k \le N, \quad \forall \Psi = (\psi_j)_{1\le j\le N} \in \mathcal{V}, \quad \sum_{j=1}^N \langle K_{ij}^0 \psi_j, \phi_k^0 \rangle = \sum_{j=1}^N \langle K_{kj}^0 \psi_j, \phi_i^0 \rangle,$$

we have in fact $\mathscr{H}\widetilde{\Psi} - \widetilde{F} \in \mathbb{S}\Phi^0$. Setting $\Psi' = \widetilde{\Psi} + S\Phi^0$, we get $\mathscr{H}\Psi' - F \in \mathbb{S}\Phi^0$. We now observe that $\mathscr{H}$ is an isomorphism from $\mathbb{A}\Phi^0$ to $\mathbb{S}^0\Phi^0$. Decomposing $\mathscr{H}\Psi' - F$ as $\mathscr{H}\Psi' - F = -S'\Phi^0 + \eta\Phi^0$ with $S' \in \mathbb{S}^0$ and $\eta \in \mathbb{D}$, and denoting by A the unique element of $\mathbb{A}$ such that $\mathscr{H}(A\Phi^0) = S'\Phi^0$, and by $\Psi = \Psi' + A\Phi^0$, we finally obtain that the pair (Ψ, η) is the unique solution to (2.55) in $\mathcal{V} \times \mathbb{D}$.

The fact that $\Psi \in (H^2(\mathbb{R}^3))^N$ whenever $f \in (L^2(\mathbb{R}^3))^N$ follows from simple elliptic regularity arguments.

To prove (2.18), we introduce, for $k \in \mathbb{N}^*$,

$$\chi_{i,k}(\beta) = \sum_{l=0}^k \beta^l \phi_{\beta W,i}^{(l)}, \quad \eta_{i,k}(\beta) = \sum_{l=0}^k \beta^l \epsilon_{\beta W,i}^{(l)},$$

$$H_k(\beta) = -\frac{1}{2}\Delta + V + \left(\sum_{i=1}^N \chi_{i,k}(\beta)^2 \right) \star |\cdot|^{-1} + \beta W, \quad f_{i,k}(\beta) = H_k(\beta)\chi_{i,k}(\beta) - \eta_{i,k}(\beta)\chi_{i,k}(\beta).$$

By construction, $|\eta_{i,k}(\beta) - \epsilon_{\beta W,i}| + \|\chi_{i,k}(\beta) - \phi_{\beta W,i}\|_{H^2} + \|f_{i,k}(\beta)\|_{H^{-1}} \in \mathcal{O}(\beta^{k+1})$ when β goes to zero, for all $1 \le i \le N$. As the operator $H_k(\beta)$ is self-adjoint, it holds

$$\langle f_{i,k}, \chi_{j,k} \rangle + \eta_{i,k}\langle \chi_{i,k}, \chi_{j,k} \rangle = \langle H_k\chi_{i,k}, \chi_{j,k} \rangle = \langle H_k\chi_{j,k}, \chi_{i,k} \rangle = \langle f_{j,k}, \chi_{i,k} \rangle + \eta_{j,k}\langle \chi_{j,k}, \chi_{i,k} \rangle$$

(the variable β has been omitted in the above equalities). As by assumption $\epsilon_1 < \epsilon_2 < \cdots < \epsilon_{N+1}$, we obtain

$$\langle \chi_{i,k}(\beta), \chi_{j,k}(\beta) \rangle = \frac{\langle f_{i,k}(\beta), \chi_{j,k}(\beta) \rangle - \langle f_{j,k}(\beta), \chi_{i,k}(\beta) \rangle}{\eta_{j,k}(\beta) - \eta_{i,k}(\beta)} \in \mathcal{O}(\beta^{k+1}),$$

from which we deduce (2.18).

2.6.7 Proof of Lemma 7

Let $T \in \Omega$ and $\gamma \in \mathcal{P}_N$ such that $\|T-\gamma\|_{\mathfrak{S}_2} < 1/2$. As $\|T-\gamma\| \leq \|T-\gamma\|_{\mathfrak{S}_2} < 1/2$, $\sigma(\gamma) = \{0,1\}$ and $\mathrm{Rank}(\gamma) = N$, $\mathrm{Rank}(\Pi(T)) = \mathrm{Rank}(\mathbb{1}_{[1/2,+\infty)}(T)) = N$. Therefore $\Pi(T) \in \mathcal{P}_N$. If, in addition, $T \in \mathfrak{S}_2$, then

$$\begin{aligned}
\|T-\Pi(T)\|_{\mathfrak{S}_2}^2 &= \|T-\gamma+\gamma-\Pi(T)\|_{\mathfrak{S}_2}^2 \\
&= \|T-\gamma\|_{\mathfrak{S}_2}^2 + \|\gamma-\Pi(T)\|_{\mathfrak{S}_2}^2 + 2\mathrm{Tr}\,((T-\gamma)(\gamma-\Pi(T))) \\
&= \|T-\gamma\|_{\mathfrak{S}_2}^2 + \|\gamma-\Pi(T)\|_{\mathfrak{S}_2}^2 + 2\mathrm{Tr}\,(T(\gamma-\Pi(T))) - (2N - 2\mathrm{Tr}\,(\gamma\Pi(T))) \\
&= \|T-\gamma\|_{\mathfrak{S}_2}^2 + 2\,\mathrm{Tr}\,(T(\gamma-\Pi(T))) \\
&= \|T-\gamma\|_{\mathfrak{S}_2}^2 + 2\,\mathrm{Tr}\,((T-1/2)(\gamma-\Pi(T)))\,,
\end{aligned}$$

where we have used that both γ and $\Pi(T)$ are in $\mathcal{P}_N$ and that for all $P \in \mathcal{P}_N$, $\|P\|_{\mathfrak{S}_2}^2 = \mathrm{Tr}\,(P^2) = \mathrm{Tr}\,(P) = N$. Let $A = T - 1/2$ and $Q = \gamma - \Pi(T)$. The self-adjoint operator A has exactly N positive eigenvalues (counting multiplicities), and all its other eigenvalues are negative. Remarking that $\Pi(T) = \mathbb{1}_{[0,+\infty)}(A)$, and denoting $A^{++} = \Pi(T)A\Pi(T)$, $A^{--} = (1-\Pi(T))A(1-\Pi(T))$, $Q^{--} = \Pi(T)(\gamma-\Pi(T))\Pi(T)$, $Q^{++} = (1-\Pi(T))(\gamma-\Pi(T))(1-\Pi(T))$, and $g := \mathrm{dist}(0,\sigma(A))$, we obtain, using the fact that $A^{++} \geq g$, $A^{--} \leq -g$, $Q^{++} \geq 0$, $Q^{--} \leq 0$ and $Q^2 = Q^{++} - Q^{--}$,

$$\begin{aligned}
\mathrm{Tr}\,((T-1/2)(\gamma-\Pi(T))) &= \mathrm{Tr}\,(A^{++}Q^{--} + A^{--}Q^{++}) \\
&\leq -g\mathrm{Tr}\,(Q^{++} - Q^{--}) = -g\mathrm{Tr}\,(Q^2) = -g\|\gamma-\Pi(T)\|_{\mathfrak{S}_2}^2.
\end{aligned}$$

Hence, $\Pi(T)$ is the unique minimizer of (2.19).

2.6.8 Proof of Theorem 8

Throughout the proof, W is a fixed potential of $\mathcal{C}'$, chosen once and for all, and C denotes a constant depending on W but not on β, which may vary from one line to another. For all $\beta \in \mathbb{R}$, we denote by $Q_W^{(n)}(\beta) := \widetilde{\gamma}_W^{(n)}(\beta) - \gamma_{\beta W}$. When $|\beta|$ is small enough, $\widetilde{\gamma}_W^{(n)}(\beta) \in \mathcal{P}_N$, so that we have

$$\begin{aligned}
E^{\mathrm{rHF}}(\widetilde{\gamma}_W^{(n)}(\beta), \beta W) &\geq \mathcal{E}^{\mathrm{rHF}}(\beta W) \\
&= E^{\mathrm{rHF}}(\gamma_{\beta W}, \beta W) \\
&= E^{\mathrm{rHF}}(\widetilde{\gamma}_W^{(n)}(\beta) - Q_W^{(n)}(\beta), \beta W) \\
&= E^{\mathrm{rHF}}(\widetilde{\gamma}_W^{(n)}(\beta), \beta W) - \mathrm{Tr}\,\left(H_{\beta W} Q_W^{(n)}(\beta)\right) - \frac{1}{2} D\left(\rho_{Q_W^{(n)}(\beta)}, \rho_{Q_W^{(n)}(\beta)}\right) \\
&= E^{\mathrm{rHF}}(\widetilde{\gamma}_W^{(n)}(\beta), \beta W) - \mathrm{Tr}\,\left(|H_{\beta W} - \epsilon_{\mathrm{F}}^0|(Q_W^{(n)}(\beta))^2\right) - \frac{1}{2}\|\rho_{Q_W^{(n)}(\beta)}\|_{\mathcal{C}}^2,
\end{aligned}$$

where we have used Lemma 18 below. We thus obtain that for $|\beta|$ small enough,

$$0 \leq E^{\mathrm{rHF}}(\widetilde{\gamma}_W^{(n)}(\beta), \beta W) - \mathcal{E}^{\mathrm{rHF}}(\beta W) = \mathrm{Tr}\,\left(|H_{\beta W} - \epsilon_{\mathrm{F}}^0|(Q_W^{(n)}(\beta))^2\right) + \frac{1}{2}\|\rho_{Q_W^{(n)}(\beta)}\|_{\mathcal{C}}^2.$$

Using (2.51), (2.52) and the bound $\|v(1-\Delta)^{-1}\| \leq C\|v\|_{\mathcal{C}'}$ for all $v \in \mathcal{C}'$, we obtain that for all $|\beta|$ small enough,

$$|H_{\beta W} - \epsilon_{\mathrm{F}}^0| \leq C(1-\Delta).$$

Hence, for $|\beta|$ small enough,

$$0 \leq E^{\mathrm{rHF}}(\widetilde{\gamma}_W^{(n)}(\beta), \beta W) - \mathcal{E}^{\mathrm{rHF}}(\beta W) \leq C\mathrm{Tr}\left((1-\Delta)(Q_W^{(n)}(\beta))^2\right) + \frac{1}{2}\|\rho_{Q_W^{(n)}(\beta)}\|_{\mathcal{C}}^2 \leq C\|Q_W^{(n)}(\beta)\|_{\mathfrak{S}_{1,1}}^2,$$

where we have used the continuity of the linear mapping $\mathfrak{S}_{1,1} \ni \gamma \mapsto \rho_\gamma \in \mathcal{C}$. The latter property is proved as followed: we infer from the Kato-Seiler-Simon inequality and the Sobolev inequality $\|V\|_{L^6(\mathbb{R}^3)} \leq C_6\|\nabla V\|_{L^2(\mathbb{R}^3)} = C_6\|V\|_{\mathcal{C}'}$ that there exists a constant $C \in \mathbb{R}_+$ such that for all $\gamma \in \mathfrak{S}_{1,1} \cap \mathcal{S}(L^2(\mathbb{R}^3))$,

$$\|\rho_\gamma\|_{\mathcal{C}} = \sup_{V \in \mathcal{C}'\setminus\{0\}} \frac{\mathrm{Tr}\,(\gamma V)}{\|V\|_{\mathcal{C}'}} = \sup_{V \in \mathcal{C}'\setminus\{0\}} \frac{\mathrm{Tr}\,((1-\Delta)^{1/2}\gamma(1-\Delta)^{1/2}(1-\Delta)^{-1/2}V(1-\Delta)^{-1/2})}{\|V\|_{\mathcal{C}'}} \leq C\|\gamma\|_{\mathfrak{S}_{1,1}}. \tag{2.56}$$

Denoting by

$$\gamma_{W,n}(\beta) := \gamma_0 + \sum_{k=1}^{n} \beta^k \gamma_W^{(k)},$$

we get

$$0 \leq E^{\mathrm{rHF}}(\widetilde{\gamma}_W^{(n)}(\beta), \beta W) - \mathcal{E}^{\mathrm{rHF}}(\beta W) \leq C\left(\|\widetilde{\gamma}_W^{(n)}(\beta) - \gamma_{W,n}(\beta)\|_{\mathfrak{S}_{1,1}}^2 + \|\gamma_{W,n}(\beta) - \gamma_{\beta W}\|_{\mathfrak{S}_{1,1}}^2\right).$$

We infer from the third statement of Theorem 5 that

$$\|\gamma_{W,n}(\beta) - \gamma_{\beta W}\|_{\mathfrak{S}_{1,1}} \leq C\beta^{n+1}.$$

We now observe that as W is fixed, all the functions $\widetilde{\phi}_{W,i}(\beta)$ in (2.21)-(2.22) lay in a finite dimensional subspace of $H^1(\mathbb{R}^3)$ independent of β. Using the equivalence of norms in finite dimension, the fact that $\widetilde{\gamma}_W^{(n)}(\beta) = \Pi\left(\gamma_{W,n}(\beta)\right)$ and Lemma 7, we obtain that

$$\|\widetilde{\gamma}_W^{(n)}(\beta) - \gamma_{W,n}(\beta)\|_{\mathfrak{S}_{1,1}} \leq C\|\widetilde{\gamma}_W^{(n)}(\beta) - \gamma_{W,n}(\beta)\|_{\mathfrak{S}_2} \leq C\|\gamma_{\beta W} - \gamma_{W,n}(\beta)\|_{\mathfrak{S}_2} \leq C\beta^{n+1},$$

which completes the proof of (2.20).

Lemma 18. *Let H be a bounded below self-adjoint operator on a Hilbert space $\mathcal{H}$, $\epsilon_{\mathrm{F}} \in \mathbb{R}$, and $\gamma := \mathbb{1}_{(-\infty,\epsilon_{\mathrm{F}}]}(H)$. Assume that $\mathrm{Tr}\,(\gamma) < \infty$. Then, for all orthogonal projector $\gamma' \in \mathcal{S}(\mathcal{H})$ such that $\mathrm{Tr}\,(\gamma') = \mathrm{Tr}\,(\gamma)$, it holds*

$$0 \leq \mathrm{Tr}\,(HQ) = \mathrm{Tr}\,(|H - \epsilon_{\mathrm{F}}|Q^2),$$

where $Q = \gamma' - \gamma$.

Proof. We first observe that

$$Q = \gamma' - \gamma = (\gamma')^2 - \gamma^2 = Q^2 + \gamma\gamma' + \gamma'\gamma - 2\gamma,$$

$$H - \epsilon_{\mathrm{F}} = (1-\gamma)(H-\epsilon_{\mathrm{F}})(1-\gamma) + \gamma(H-\epsilon_{\mathrm{F}})\gamma,$$

$$|H-\epsilon_{\rm F}| = (1-\gamma)(H-\epsilon_{\rm F})(1-\gamma) - \gamma(H-\epsilon_{\rm F})\gamma,$$
$$Q^2 = (1-\gamma)Q(1-\gamma) - \gamma Q\gamma.$$

As $\mathrm{Tr}\,(Q)=0$, it follows that

$$\begin{aligned}
\mathrm{Tr}\,(HQ) &= \mathrm{Tr}\,((H-\epsilon_{\rm F})Q) = \mathrm{Tr}\,\left((H-\epsilon_{\rm F})Q^2\right) + \mathrm{Tr}\,\left((H-\epsilon_{\rm F})(\gamma\gamma'+\gamma'\gamma-2\gamma)\right)\\
&= \mathrm{Tr}\,\left((H-\epsilon_{\rm F})Q^2\right) + 2\,\mathrm{Tr}\,\left(\gamma(H-\epsilon_{\rm F})\gamma Q\right)\\
&= \mathrm{Tr}\,\left((H-\epsilon_{\rm F})Q^2\right) + 2\,\mathrm{Tr}\,\left(\gamma(H-\epsilon_{\rm F})\gamma Q\gamma\right)\\
&= \mathrm{Tr}\,\left((H-\epsilon_{\rm F})Q^2\right) - 2\,\mathrm{Tr}\,\left(\gamma(H-\epsilon_{\rm F})\gamma Q^2\right)\\
&= \mathrm{Tr}\,\left(|H-\epsilon_{\rm F}|Q^2\right).
\end{aligned}$$

Note that all the terms in the above series of equalities containing γ are finite, since $\mathrm{Tr}\,(\gamma)<\infty$ and H is bounded below, while the other terms may be equal to $+\infty$. □

2.6.9 Proof of Lemma 9

Using the fact that $L^2(\mathbb{R}^3) = \mathcal{H}_{\rm o}\oplus\mathcal{H}_{\rm u}$, any linear operator T on $L^2(\mathbb{R}^3)$ can be represented by a 2×2 block operator

$$T = \begin{pmatrix} T_{\rm oo} & T_{\rm ou} \\ T_{\rm uo} & T_{\rm uu} \end{pmatrix},$$

where $T_{\rm xy}$ is a linear operator from $\mathcal{H}_{\rm y}$ to $\mathcal{H}_{\rm x}$ (with $x,y\in\{\mathrm{o},\mathrm{u}\}$). In particular, the operators $P_0 := \mathbb{1}_{(-\infty,\epsilon_{\rm F}^0]}(H_0)$ (the orthogonal projector on $\mathcal{H}_{\rm o}$), $P_0^\perp := \mathbb{1}_{(\epsilon_{\rm F}^0,+\infty)}(H_0)$ and H_0 are block diagonal in this representation, and we have

$$P_0 = \begin{pmatrix} 1 & 0 \\ 0 & 0 \end{pmatrix}, \qquad P_0^\perp = \begin{pmatrix} 0 & 0 \\ 0 & 1 \end{pmatrix}, \qquad H_0 = \begin{pmatrix} H_{\rm oo} & 0 \\ 0 & H_{\rm uu} \end{pmatrix},$$

with $H_{\rm oo}-\epsilon_{\rm F}^0\leq 0$ and $H_{\rm uu}-\epsilon_{\rm F}^0 = H_0^{++}-\epsilon_{\rm F}^0 \geq g_+ > 0$.

We consider the submanifold

$$\mathcal{P}_{N_{\rm o}} := \left\{P\in\mathcal{S}(L^2(\mathbb{R}^3)) \mid P^2=P,\ \mathrm{Tr}\,(P)=N_{\rm o},\ \mathrm{Tr}\,(-\Delta P)<\infty\right\}$$

of $\mathcal{S}(L^2(\mathbb{R}^3))$ consisting of the rank-$N_{\rm o}$ orthogonal projectors on $L^2(\mathbb{R}^3)$ with range in $H^1(\mathbb{R}^3)$, and the Hilbert space

$$\mathcal{Z} = \left\{ Z = \begin{pmatrix} 0 & -Z_{\rm uo}^* \\ Z_{\rm uo} & 0 \end{pmatrix} \mid (H_{\rm uu}-\epsilon_{\rm F}^0)^{1/2} Z_{\rm uo} \in \mathcal{B}(\mathcal{H}_{\rm o},\mathcal{H}_{\rm u}) \right\},$$

endowed with the inner product

$$(Z,Z')_{\mathcal{Z}} = \mathrm{Tr}\,(Z_{\rm uo}^*(H_{\rm uu}-\epsilon_{\rm F}^0)Z'_{\rm uo}).$$

We are going to use the following lemma, the proof of which is postponed until the end of the section.

Lemma 19. *There exists an open connected neighborhood $\widetilde{\mathcal{O}}$ of P_0 in $\mathcal{P}_{N_\mathrm{o}}$, and $\eta > 0$ such that the real analytic mapping*

$$\begin{aligned} B_\eta(\mathcal{Z}) &\to \widetilde{\mathcal{O}} \\ Z &\mapsto e^Z P_0 e^{-Z} \end{aligned}$$

is bijective.

By continuity, there exists a neighborhood $\mathcal{O}$ of 0 in $\mathcal{A}$ such that

$$\forall A \in \mathcal{O}, \quad \mathbb{1}_{(0,1]}\left(\Gamma(A)\right) \subset \widetilde{\mathcal{O}}.$$

Let A and A' in $\mathcal{O}$ be such that $\Gamma(A) = \Gamma(A')$. Then

$$e^{L_{\mathrm{uo}}(A')} P_0 e^{-L_{\mathrm{uo}}(A')} = \mathbb{1}_{(0,1]}\left(\Gamma(A')\right) = \mathbb{1}_{(0,1]}\left(\Gamma(A)\right) = e^{L_{\mathrm{uo}}(A)} P_0 e^{-L_{\mathrm{uo}}(A)},$$

and we infer from Lemma 19 that $L_{\mathrm{uo}}(A') = L_{\mathrm{uo}}(A)$. Therefore,

$$e^{L_{\mathrm{pf}}(A')}(\gamma_0 + L_{\mathrm{pp}}(A'))e^{-L_{\mathrm{pf}}(A')} = e^{L_{\mathrm{pf}}(A)}(\gamma_0 + L_{\mathrm{pp}}(A))e^{-L_{\mathrm{pf}}(A)}. \tag{2.57}$$

In particular (using again functional calculus),

$$e^{L_{\mathrm{pf}}(A')}\gamma_0 e^{-L_{\mathrm{pf}}(A')} = e^{L_{\mathrm{pf}}(A)}\gamma_0 e^{-L_{\mathrm{pf}}(A)}.$$

Using the finite dimensional analogue of Lemma 19 (a standard result on finite dimensional Grassmann manifolds), we obtain that, up to reducing the size of the neighborhood $\mathcal{O}$ if necessary, $L_{\mathrm{pf}}(A') = L_{\mathrm{pf}}(A)$. Getting back to (2.57), we see that $L_{\mathrm{pp}}(A') = L_{\mathrm{pp}}(A)$. Therefore, $A = A'$, which proves the injectivity of the mapping (2.26).

We now consider a neighborhood $\mathcal{O}'$ of γ_0 in $\mathfrak{S}_{1,1}$ in such that $\Gamma(\mathcal{O}) \subset \mathcal{O}'$ and $\mathbb{1}_{(0,1]}\left(\mathcal{K}_{N_\mathrm{f},N_\mathrm{p}} \cap \mathcal{O}'\right) \subset \widetilde{\mathcal{O}}$. Let $\gamma \in \mathcal{K}_{N_\mathrm{f},N_\mathrm{p}} \cap \mathcal{O}'$. By Lemma 19, there exists a unique $Z \in B_\eta(\mathcal{Z})$ such that $\mathbb{1}_{(0,1]}(\gamma) = e^Z P_0 e^{-Z}$, and by the classical finite-dimensional version of the latter lemma, there exists a unique $A_{\mathrm{pf}} \in \mathcal{A}_{\mathrm{pf}}$ in the vicinity of 0 such that $\mathbb{1}_{\{1\}}(\gamma) = e^Z e^{L_{\mathrm{pf}}(0,0,A_{\mathrm{pf}},0)} \mathbb{1}_{\{1\}}(\gamma_0) e^{-L_{\mathrm{pf}}(0,0,A_{\mathrm{pf}},0)} e^{-Z}$. It is then easily seen that the operator

$$e^{-Z} e^{-L_{\mathrm{pf}}(0,0,A_{\mathrm{pf}},0)} \gamma e^{L_{\mathrm{pf}}(0,0,A_{\mathrm{pf}},0)} e^{Z}$$

is of the form $\gamma_0 + L_{\mathrm{pp}}(0,0,0,A_{\mathrm{pp}})$ for some $A_{\mathrm{pp}} \in \mathcal{A}_{\mathrm{pp}}$, which is close to 0 if $\mathcal{O}'$ is small enough. Decomposing Z_{uo} as $(A_{\mathrm{uf}}, A_{\mathrm{up}})$ and setting $A = (A_{\mathrm{uf}}, A_{\mathrm{up}}, A_{\mathrm{pf}}, A_{\mathrm{pp}})$, we obtain that A is the unique element of $\mathcal{A}$ in the vicinity of 0 such that $\gamma = \Gamma(A)$.

Proof of Lemma 19. Let

$$\mathcal{U} := \left\{U \in \mathrm{GL}(H^1(\mathbb{R}^3)) \mid \|U\phi\|_{L^2} = \|\phi\|_{L^2},\ \forall \phi \in H^1(\mathbb{R}^3)\right\}$$

where $\mathrm{GL}(H^1(\mathbb{R}^3))$ is the group of the inversible bounded operators on $H^1(\mathbb{R}^3)$. In view of [26, Theorem 4.8], the mapping

$$\begin{aligned} \mathcal{U} &\to \mathcal{P}_{N_\mathrm{o}} \\ U &\mapsto U P_0 U^{-1} \end{aligned}$$

is a real analytic submersion. Besides [26, Lemma 2.5], $\mathcal{U}$ is a Banach-Lie group with Lie algebra

$$\mathscr{U} = \left\{ Z \in \mathcal{B}(L^2(\mathbb{R}^3)) \mid Z^* = -Z,\ Z(H^1(\mathbb{R}^3)) \subset H^1(\mathbb{R}^3) \right\}$$

(with the slight abuse of notation consisting of denoting by Z the restriction to $H^1(\mathbb{R}^3)$ of an operator $Z \in \mathcal{B}(L^2(\mathbb{R}^3))$ such that $Z(H^1(\mathbb{R}^3)) \subset H^1(\mathbb{R}^3)$), and [26, Remark 4.7], the isotropy group of the action of $\mathcal{U}$ on $\mathcal{P}_{N_\mathrm{o}}$ is the Banach-Lie group with Lie algebra

$$\mathscr{U}_0 = \left\{ Z \in \mathcal{B}(L^2(\mathbb{R}^3)) \mid Z^* = -Z,\ Z(H^1(\mathbb{R}^3)) \subset H^1(\mathbb{R}^3),\ Z_{\mathrm{uo}} = 0 \right\}.$$

Hence, denoting by

$$\widetilde{\mathcal{Z}} = \left\{ Z = \begin{pmatrix} 0 & -Z_{\mathrm{uo}}^* \\ Z_{\mathrm{uo}} & 0 \end{pmatrix} \mid (1-\Delta)^{1/2} Z_{\mathrm{uo}} \in \mathcal{B}(\mathcal{H}_\mathrm{o}, \mathcal{H}_\mathrm{u}) \right\},$$

there exists an open connected neighborhood $\widetilde{\mathcal{O}}$ of P_0 in $\mathcal{P}_{N_\mathrm{o}}$, and $\widetilde{\eta} > 0$ such that the real analytic mapping

$$\begin{aligned} B_{\widetilde{\eta}}(\widetilde{\mathcal{Z}}) &\to \widetilde{\mathcal{O}} \\ Z &\mapsto e^Z P_0 e^{-Z} \end{aligned}$$

is bijective. As there exists $0 < c < C < \infty$ such that $c(1-\Delta) \leq (H_{\mathrm{uu}} - \epsilon_\mathrm{F}^0) \leq C(1-\Delta)$ on $\mathcal{H}_\mathrm{u}$, we have $\widetilde{\mathcal{Z}} = \mathcal{Z}$, which concludes the proof of the lemma. □

2.6.10 Proof of Lemma 10

In view of (2.33), the density matrix $\Gamma(A)$ can be expanded as

$$\Gamma(A) = \gamma_0 + \gamma_1(A) + \gamma_2(A,A) + O(\|A\|_{\mathcal{V}}^3), \tag{2.58}$$

with

$$\begin{aligned} \gamma_1(A) &= \langle \Gamma'(0), A \rangle = [L_{\mathrm{uo}}(A) + L_{\mathrm{pf}}(A), \gamma_0] + L_{\mathrm{pp}}(A) \\ \gamma_2(A,A) &= \frac{1}{2}[\Gamma''(0)](A,A) \\ &= \frac{1}{2}\left[L_{\mathrm{uo}}(A), [L_{\mathrm{uo}}(A), \gamma_0]\right] + \left[L_{\mathrm{uo}}(A), [L_{\mathrm{pf}}(A), \gamma_0]\right] + \frac{1}{2}\left[L_{\mathrm{pf}}(A), [L_{\mathrm{pf}}(A), \gamma_0]\right] \\ &\quad + [L_{\mathrm{uo}}(A), L_{\mathrm{pp}}(A)] + [L_{\mathrm{pf}}(A), L_{\mathrm{pp}}(A)] \\ &= \frac{1}{2}\left\{ L_{\mathrm{uo}}(A)^2 + L_{\mathrm{pf}}(A)^2, \gamma_0 \right\} + [L_{\mathrm{uo}}(A) + L_{\mathrm{pf}}(A), L_{\mathrm{pp}}(A)] \\ &\quad + L_{\mathrm{uo}}(A) L_{\mathrm{pf}}(A) \gamma_0 + \gamma_0 L_{\mathrm{pf}}(A) L_{\mathrm{uo}}(A) - (L_{\mathrm{uo}}(A) + L_{\mathrm{pf}}(A)) \gamma_0 (L_{\mathrm{uo}}(A) + L_{\mathrm{pf}}(A)), \end{aligned}$$

where $\{X, Y\} = XY + YX$ denotes the anticommutator of X and Y. As in Section 2.4, we denote by $F(A,0) = \nabla_A E(A,0)$ and $\Theta = \frac{1}{2} F'_A(0,0)|_{\mathcal{A}\times\{0\}}$. It follows from (2.58) and the analyticity properties of the mapping $A \mapsto E(A,0)$ that for all $(A, A') \in \mathcal{A} \times \mathcal{A}$,

$$E(A,0) = E_0 + \mathrm{Tr}\left(H_0 \gamma_1(A)\right) + \mathrm{Tr}\left(H_0 \gamma_2(A,A)\right) + \frac{1}{2} D(\rho_{\gamma_1(A)}, \rho_{\gamma_1(A)}) + O(\|A\|_{\mathcal{A}}^3),$$

and

$$\langle \Theta(A), A \rangle = \mathrm{Tr}\left(H_0 \gamma_2(A,A)\right) + \frac{1}{2} D(\rho_{\gamma_1(A)}, \rho_{\gamma_1(A)}).$$

Besides, a simple calculation leads to

$$\begin{aligned}\mathrm{Tr}\left(H_0\gamma_2(A,A)\right) &= \mathrm{Tr}\left(A_{\rm uf}^*\left(H_0^{++}-\epsilon_{\rm F}^0\right)A_{\rm uf}\right)-\mathrm{Tr}\left(A_{\rm uf}\left(H_0^{--}-\epsilon_{\rm F}^0\right)A_{\rm uf}^*\right)\\ &\quad+\mathrm{Tr}\left(\left(H_0^{++}-\epsilon_{\rm F}^0\right)A_{\rm up}\Lambda A_{\rm up}^*\right)-\mathrm{Tr}\left(\left(H_0^{--}-\epsilon_{\rm F}^0\right)A_{\rm pf}^*(1-\Lambda)A_{\rm pf}\right).\end{aligned}$$

Hence,

$$\langle\Theta(A),A'\rangle = a(A,A')+\frac{1}{2}D(\rho_{\gamma_1(A)},\rho_{\gamma_1(A')}), \tag{2.59}$$

where

$$\begin{aligned}a(A,A') &= \mathrm{Tr}\left(A_{\rm uf}^*\left(H_0^{++}-\epsilon_{\rm F}^0\right)A'_{\rm uf}\right)-\mathrm{Tr}\left(A'_{\rm uf}\left(H_0^{--}-\epsilon_{\rm F}^0\right)A_{\rm uf}^*\right)\\ &\quad+\mathrm{Tr}\left(\left(H_0^{++}-\epsilon_{\rm F}^0\right)A'_{\rm up}\Lambda A_{\rm up}^*\right)-\mathrm{Tr}\left(\left(H_0^{--}-\epsilon_{\rm F}^0\right)A_{\rm pf}^*(1-\Lambda)A'_{\rm pf}\right).\end{aligned}$$

For all A and A' in $\mathcal{A}$, we have

$$|a(A,A')| \leq \left(1+\frac{\epsilon_{\rm F}^0-\epsilon_1}{g_+}\right)\|A_{\rm uf}\|_{\mathcal{A}_{\rm uf}}\|A'_{\rm uf}\|_{\mathcal{A}_{\rm uf}}+\|A_{\rm up}\|_{\mathcal{A}_{up}}\|A'_{\rm up}\|_{\mathcal{A}_{\rm up}}+(\epsilon_{\rm F}^0-\epsilon_1)\|A_{\rm pf}\|_{\mathcal{A}_{\rm pf}}\|A'_{\rm pf}\|_{\mathcal{A}_{\rm pf}}.$$

We thus deduce from (2.56) that there exists a constant $C'\in\mathbb{R}_+$ such that for all $A\in\mathcal{A}$,

$$\|\rho_{\gamma_1(A)}\|_{\mathcal{C}} \leq C\|\gamma_1(A)\|_{\mathfrak{S}_{1,1}} \leq C'\|A\|_{\mathcal{A}}.$$

The bilinear form in (2.59) is therefore continuous on the Hilbert space $\mathcal{A}$. It is also positive since for all $A\in\mathcal{A}$,

$$\langle\Theta(A),A\rangle \geq \|A_{\rm uf}\|_{\mathcal{A}_{\rm uf}}^2+\lambda_-\|A_{\rm up}\|_{\mathcal{A}_{\rm up}}^2+(1-\lambda_+)g_-\|A_{\rm pf}\|_{\mathcal{A}_{\rm pf}}^2+\frac{1}{2}\|\rho_{\gamma_1(A)}\|_{\mathcal{C}}^2, \tag{2.60}$$

where $0<\lambda_-\leq\lambda_+<1$ are the lowest and highest eigenvalues of Λ. To prove that it is in fact coercive, we proceed by contradiction and assume that there exists a normalized sequence $(A_k)_{k\in\mathbb{N}}$ in $\mathcal{A}$ such that $\lim_{k\to\infty}\langle\Theta(A_k),A_k\rangle=0$. We infer from (2.60) that $\|(A_k)_{\rm uf}\|_{\mathcal{A}_{\rm uf}}$, $\|(A_k)_{\rm up}\|_{\mathcal{A}_{\rm up}}$, $\|(A_k)_{\rm pf}\|_{\mathcal{A}_{\rm pf}}$ and $\|\rho_{\gamma_1(A_k)}\|_{\mathcal{C}}$ converge to zero when k goes to infinity. Denoting by $(M_k)_{ij}:=(\phi^0_{N_{\rm f}+i},(A_k)_{\rm pp}\phi^0_{N_{\rm f}+j})_{L^2}$, this implies that $\|M_k\|_2=\|(A_k)_{\rm pp}\|_{\mathcal{A}_{\rm pp}}\to 1$ and

$$\left\|\sum_{i,j=1}^{N_{\rm p}}(M_k)_{ij}\phi^0_{N_{\rm f}+i}\phi^0_{N_{\rm f}+j}\right\|_{\mathcal{C}}\to 0.$$

Extracting from $(M_k)_{k\in\mathbb{N}}$ a subsequence $(M_{k_n})_{n\in\mathbb{N}}$ converging to some $M\in\mathbb{R}_{\rm S}^{N_{\rm p}\times N_{\rm p}}$, and letting n go to infinity, we obtain

$$\|M\|_2=1 \qquad \text{and} \qquad \sum_{i,j=1}^{N_{\rm p}}M_{ij}\phi^0_{N_{\rm f}+i}\phi^0_{N_{\rm f}+j}=0.$$

This contradicts (2.9). The bilinear form (2.59) is therefore coercive on $\mathcal{A}$. As it is also continuous, we obtain that the linear map Θ is a bicontinuous coercive isomorphism from $\mathcal{A}$ to $\mathcal{A}'$.

2.6.11 Proof of Lemma 11

We can prove the existence of a minimizer $\widetilde{\gamma}_W$ to (2.4) reasoning as in the proof of the first statement of Theorem 5 (non-degenerate case) up to (2.52). Only the final argument is slightly different. In the degenerate case, we deduce that H_W has at least N negative eigenvalues from the fact that $\mathrm{Rank}(\mathbb{1}_{(-\infty,\alpha_5]}(H_W)) = N_\mathrm{o} \geq N$.

We now have to prove that $\widetilde{\gamma}_W = \gamma_W$, where γ_W is defined by (2.29). We know that γ_W is the unique local minimizer of (2.24) in the neighborhood of γ_0. Decomposing the space $L^2(\mathbb{R}^3)$ as

$$L^2(\mathbb{R}^3) = \mathcal{H}_\mathrm{f}^W \oplus \mathcal{H}_\mathrm{p}^W \oplus \mathcal{H}_\mathrm{u}^W, \tag{2.61}$$

where $\mathcal{H}_\mathrm{f}^W = \mathrm{Ran}(\mathbb{1}_{\{1\}}(\gamma_W))$, $\mathcal{H}_\mathrm{p}^W = \mathrm{Ran}(\mathbb{1}_{(0,1)}(\gamma_W))$, and $\mathcal{H}_\mathrm{u}^W = \mathrm{Ran}(\mathbb{1}_{\{0\}}(\gamma_W))$, we can parametrize $\mathcal{K}_{N_\mathrm{f},N_\mathrm{p}}$ in the neighborhood of γ_W using the local map

$$\Gamma^W(A) := \exp\left(L_\mathrm{uo}^W(A)\right)\, \exp\left(L_\mathrm{pf}^W(A)\right)\, \left(\gamma_W + L_\mathrm{pp}^W(A)\right)\, \exp\left(-L_\mathrm{pf}^W(A)\right)\, \exp\left(-L_\mathrm{uo}^W(A)\right),$$

where

$$L_\mathrm{uo}^W(A) := \begin{bmatrix} 0 & 0 & -A_\mathrm{uf}^* \\ 0 & 0 & -A_\mathrm{up}^* \\ A_\mathrm{uf} & A_\mathrm{up} & 0 \end{bmatrix}, \quad L_\mathrm{pf}^W(A) := \begin{bmatrix} 0 & -A_\mathrm{pf}^* & 0 \\ A_\mathrm{pf} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}, \quad L_\mathrm{pp}^W(A) := \begin{bmatrix} 0 & 0 & 0 \\ 0 & A_\mathrm{pp} & 0 \\ 0 & 0 & 0 \end{bmatrix},$$

the block decomposition of the operators $L_\mathrm{xy}^W(A)$ being done with respect to the decomposition (2.61) of the space $L^2(\mathbb{R}^3)$. As $A = 0$ is the unique minimizer of the functional $A \mapsto \mathcal{E}^\mathrm{rHF}(\Gamma^W(A), W)$ in the neighborhood of 0, we obtain that the block decomposition of the operator $\widetilde{H} = -\frac{1}{2}\Delta + V + \rho_{\gamma_W} \star |\cdot|^{-1} + W$ reads

$$\widetilde{H} := \begin{bmatrix} \widetilde{H}_\mathrm{ff} & 0 & 0 \\ 0 & \widetilde{H}_\mathrm{pp} & 0 \\ 0 & 0 & \widetilde{H}_\mathrm{uu} \end{bmatrix}$$

(first-order optimality conditions), and that there exists $\epsilon \in \mathbb{R}$ such that

$$\widetilde{H}_\mathrm{ff} - \epsilon \leq 0, \quad \widetilde{H}_\mathrm{pp} - \epsilon = 0, \quad \widetilde{H}_\mathrm{uu} - \epsilon \geq 0$$

(second-order optimality conditions). These conditions also read

$$\gamma_W = \mathbb{1}_{(-\infty,\epsilon)}(\widetilde{H}) + \delta_W, \tag{2.62}$$

with $0 \leq \delta_W \leq 1$, $\mathrm{Ran}(\delta_W) \subset \mathrm{Ker}(\widetilde{H} - \epsilon)$, $\mathrm{Tr}\,(\gamma_W) = N$, which are precisely the Euler conditions for problem (2.4). Thus, γ_W is a minimizer to (2.4).

It follows that all the minimizers $\widetilde{\gamma}_W$ of (2.4) have density $\rho_W := \rho_{\gamma_W}$ and are of the form

$$\widetilde{\gamma}_W = \mathbb{1}_{(-\infty,\epsilon)}(\widetilde{H}) + \widetilde{\delta}_W,$$

with $0 \leq \widetilde{\delta}_W \leq 1$, $\mathrm{Ran}(\widetilde{\delta}_W) \subset \mathrm{Ker}(\widetilde{H} - \epsilon)$, $\mathrm{Tr}\,(\widetilde{\gamma}_W) = N$. As the optimization problem (2.4) is convex, the set of its minimizers is convex. Therefore, for any $t \in [0,1]$

$$(1-t)\gamma_W + t\widetilde{\gamma}_W = \mathbb{1}_{(-\infty,\epsilon)}(\widetilde{H}) + (1-t)\delta_W + t\widetilde{\delta}_W,$$

is a global minimizer of (2.4), hence of (2.24) for t small enough. As we know that γ_W is the unique minimizer to (2.24) in the vicinity of γ_0, we obtain that $\widetilde{\delta}_W = \delta_W$, which proves that γ_W is the unique minimizer of (2.4).

2.6.12 Proof of Theorem 12

The first statement of Theorem 12 has been proved in the previous section. The second statement is a consequence of (2.62) and of the fact that $\gamma_W \in \mathcal{K}_{N_{\mathrm{f}},N_{\mathrm{p}}}$. The third statement follows from the real analyticity of the mappings $B_\eta(\mathcal{C}') \ni W \mapsto \widetilde{A}(W) \in \mathcal{A}$, $\mathcal{A} \ni A \mapsto \Gamma(A) \in \mathfrak{S}_{1,1}$, and $\mathfrak{S}_{1,1} \times \mathcal{C}' \ni (\gamma, W) \mapsto E^{\mathrm{rHF}}(\gamma, W) \in \mathbb{R}$ and the chain rule.

It follows from (2.33) that for all $A \in \mathcal{O}$ and all $W \in \mathcal{C}'$,

$$\begin{aligned} E(A,W) &= E_0 + \int_{\mathbb{R}^3} \rho_{\gamma_0} W + \langle \Theta(A), A\rangle + \int_{\mathbb{R}^3} \rho_{\gamma_1(A)} W + \sum_{l\geq 3} \mathrm{Tr}\,(H_0 \gamma_l(A,\cdots,A)) \\ &+ \frac{1}{2} \sum_{\substack{l+l'\geq 3 \\ l,l'\geq 1}} D(\rho_{\gamma_l(A,\cdots,A)}, \rho_{\gamma_{l'}(A,\cdots,A)}) + \sum_{l\geq 2} \int_{\mathbb{R}^3} \rho_{\gamma_l(A,\cdots,A)} W. \end{aligned}$$

As a consequence, we obtain that that for any $A' \in \mathcal{O}$,

$$\begin{aligned} (\nabla_A E(A,W), A')_{\mathcal{A}} &= 2\langle \Theta(A), A'\rangle + \int_{\mathbb{R}^3} \rho_{\gamma_1(A')} W + \sum_{l\geq 3} \mathrm{Tr}\,(H_0 \Gamma_l(A,A')) \\ &+ \sum_{\substack{l+l'\geq 3 \\ l\geq 1,\ l'\geq 1}} D(\rho_{\gamma_l(A,\cdots,A)}, \rho_{\Gamma_{l'}(A,A')}) + \sum_{l\geq 2} \int_{\mathbb{R}^3} \rho_{\Gamma_l(A,A')} W, \end{aligned} \tag{2.63}$$

with where $\Gamma_1(A,A') = \gamma_1(A')$ is in fact independent of A, and where for all $l \geq 2$, $\Gamma_l(A,A') = \sum_{i=1}^{l} \gamma_l(\tau_{(i,l)}(A,\cdots,A,A'))$ (recall that $\tau_{(i,l)}$ denotes the transposition swapping the i^{th} and l^{th} elements, and that, by convention $\tau_{l,l}$ is the identity). By definition of $A_W(\beta)$, we have

$$\forall A' \in \mathcal{A}, \quad (\nabla_A E(A_W(\beta), \beta W), A')_{\mathcal{A}} = 0. \tag{2.64}$$

Using (2.63) and observing that

$$\Gamma_l(A_W(\beta), A') = \sum_{k\geq l-1} \beta^k \sum_{\substack{\alpha\in(\mathbb{N}^*)^{l-1} \\ |\alpha|_1 = k, |\alpha|_\infty < k}} \sum_{i=1}^{l} \gamma_l(\tau_{(i,l)}(A_W^{(\alpha_1)}, \cdots, A_W^{(\alpha_{l-1})}, A')), \tag{2.65}$$

we can rewrite (2.64) by collecting the terms of order β^k as

$$\forall k \in \mathbb{N}^*, \quad \forall A' \in \mathcal{A}, \quad \langle 2\Theta(A_W^{(k)}) + B_W^{(k)}, A'\rangle = 0,$$

where $B_W^{(k)}$ is given by (2.37) for $k = 1$ and by (2.38) for the general case $k \geq 2$. Thus (2.36) is proved.

Using (2.30) and (2.32), we can rewrite (2.35) for $k = 2n + \epsilon$ ($n \in \mathbb{N}$, $\epsilon \in \{0, 1\}$) as

$$\begin{aligned}
\mathcal{E}_W^{(2n+\epsilon)} &= \mathrm{Tr}\,(H_0\gamma_1(A_W^{(2n+\epsilon)})) + \sum_{2\leq l\leq 2n+\epsilon} \sum_{\alpha\in(\mathbb{N}^*)^l \,|\, |\alpha|_1=2n+\epsilon} \mathrm{Tr}\,(H_0\gamma_{W,l}^{\alpha}) \\
&+ \frac{1}{2} \sum_{\substack{2\leq l+l'\leq 2n+\epsilon \\ l,l'\geq 1}} \sum_{\alpha\in(\mathbb{N}^*)^l,\, \alpha'\in(\mathbb{N}^*)^{l'} \,|\, |\alpha|_1+|\alpha'|_1=2n+\epsilon} D(\rho_{\gamma_{W,l}^{\alpha}}, \rho_{\gamma_{W,l'}^{\alpha'}}) \\
&+ \sum_{2\leq l\leq 2n+\epsilon-1} \sum_{\alpha\in(\mathbb{N}^*)^l \,|\, |\alpha|_1=2n+\epsilon-1} \int_{\mathbb{R}^3} \rho_{\gamma_{W,l}^{\alpha}} W \\
&= \sum_{2\leq l\leq 2n+\epsilon} \sum_{\alpha\in(\mathbb{N}^*)^l \,|\, |\alpha|_1=2n+\epsilon,\, |\alpha|_\infty\leq n} \mathrm{Tr}\,(H_0\gamma_{W,l}^{\alpha}) \\
&+ \frac{1}{2} \sum_{\substack{2\leq l+l'\leq 2n+\epsilon \\ l,l'\geq 1}} \sum_{\substack{\alpha\in(\mathbb{N}^*)^l,\, \alpha'\in(\mathbb{N}^*)^{l'} \,|\, |\alpha|_1+|\alpha'|_1=2n+\epsilon \\ \max(|\alpha|_\infty,\, |\alpha'|_\infty)\leq n}} D(\rho_{\gamma_{W,l}^{\alpha}}, \rho_{\gamma_{W,l'}^{\alpha'}}) \\
&+ \sum_{2\leq l\leq 2n+\epsilon-1} \sum_{\alpha\in(\mathbb{N}^*)^l \,|\, |\alpha|_1=2n+\epsilon-1,\, |\alpha|_\infty\leq n} \int_{\mathbb{R}^3} \rho_{\gamma_{W,l}^{\alpha}} W + J_{2n+\epsilon}(A_W^{(1)}, ..., A_W^{(2n+\epsilon-1)}),
\end{aligned}$$

where

$$\begin{aligned}
J_{2n+\epsilon}(A_W^{(1)}, ..., A_W^{(2n+\epsilon-1)}) = & \sum_{2\leq l\leq 2n+\epsilon} \sum_{\substack{\alpha\in(\mathbb{N}^*)^l \,|\, |\alpha|_1=2n+\epsilon \\ |\alpha|_\infty>n}} \mathrm{Tr}\,(H_0\gamma_l^{(\alpha)}) \\
&+ \frac{1}{2} \sum_{\substack{2\leq l_1+l_2\leq 2n+\epsilon \\ l_1,l_2\geq 1}} \sum_{\substack{\alpha\in(\mathbb{N}^*)^l,\, \alpha'\in(\mathbb{N}^*)^{l'} \,|\, |\alpha|_1+|\alpha'|_1=2n+\epsilon \\ \max(|\alpha|_\infty,|\alpha'|_\infty)>n}} D(\rho_{\gamma_{l_1}^{(\alpha)}}, \rho_{\gamma_{l_2}^{(\alpha')}}) \\
&+ \sum_{1\leq l\leq 2n+\epsilon-1} \sum_{\substack{\alpha\in(\mathbb{N}^*)^l \,|\, |\alpha|_1=2n+\epsilon-1 \\ |\alpha|_\infty>n}} \int_{\mathbb{R}^3} \rho_{\gamma_l^{(\alpha)}} W.
\end{aligned}$$

As

$$J_{2n+\epsilon}(A_W^{(1)}, ..., A_W^{(2n+\epsilon-1)}) = \sum_{k=n}^{2n+\epsilon-1} \langle 2\Theta(A_W^{(2n+\epsilon-k)}) + B_W^{(2n+\epsilon-k)}, A_W^{(k)} \rangle = 0,$$

the proof of the fifth statement is complete. Lastly, the sixth statement can be established reasoning as in the proof of Theorem 8.

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2.A Second order perturbation theory

The block representation of $\gamma_W^{(2)}$, the second order perturbation expansion of the ground state energy density is given by the sum of

$$\begin{bmatrix} 0 & (A_{\rm pf}^{(2)})^*(I-\Lambda) & (A_{\rm uf}^{(2)})^* \\ (I-\Lambda)A_{\rm pf}^{(2)} & M^{(2)} & \Lambda(A_{\rm up}^{(2)})^* \\ A_{\rm uf}^{(2)} & A_{\rm up}^{(2)}\Lambda & 0 \end{bmatrix}$$

and

$$\begin{bmatrix} -(A_{\rm pf}^{(1)})^*(I-\Lambda)A_{\rm pf}^{(1)} & -\frac{1}{2}(A_{\rm uf}^{(1)})^*A_{\rm up}^{(1)}(\Lambda+I) & (A_{\rm pf}^{(1)})^*(I-\Lambda)(A_{\rm up}^{(1)})^* \\ -(A_{\rm uf}^{(1)})^*A_{\rm uf}^{(1)} & -(A_{\rm pf}^{(1)})^*A_{\rm pp}^{(1)} & \\ -\frac{1}{2}(\Lambda+I)(A_{\rm up}^{(1)})^*A_{\rm uf}^{(1)} & -\frac{1}{2}(A_{\rm up}^{(1)})^*A_{\rm up}^{(1)}\Lambda - \frac{1}{2}\Lambda(A_{\rm up}^{(1)})^*A_{\rm up}^{(1)} & (I-\Lambda)A_{\rm pf}^{(1)}(A_{\rm uf}^{(1)})^* \\ -A_{\rm pp}^{(1)}A_{\rm pf}^{(1)} & +\frac{1}{2}(I-\Lambda)A_{\rm pf}^{(1)}(A_{\rm pf}^{(1)})^* & +A_{\rm pp}^{(1)}(A_{\rm up}^{(1)})^* \\ & +\frac{1}{2}A_{\rm pf}^{(1)}(A_{\rm pf}^{(1)})^*(I-\Lambda) & \\ A_{\rm up}^{(1)}(I-\Lambda)A_{\rm pf}^{(1)} & A_{\rm uf}^{(1)}(A_{\rm pf}^{(1)})^*(I-\Lambda) & A_{\rm up}^{(1)}\Lambda(A_{\rm up}^{(1)})^* \\ & +A_{\rm up}^{(1)}A_{\rm pp}^{(1)} & +A_{\rm uf}^{(1)}(A_{\rm uf}^{(1)})^* \end{bmatrix},$$

where the above operators solve the following systems

$$\Theta\left((A_{\rm pf}^{(1)}, A_{\rm uf}^{(1)}, A_{\rm up}^{(1)}, A_{\rm pp}^{(1)})\right) = -((1-\Lambda)W_{\rm pf}, W_{\rm uf}, W_{\rm up}\Lambda, W_{\rm pp}), \tag{2.66}$$

and

$$\Theta\left((A_{\rm pf}^{(2)}, A_{\rm uf}^{(2)}, A_{\rm up}^{(2)}, A_{\rm pp}^{(2)})\right) = -\frac{1}{2}((B_{\rm pf}^{(2)}, B_{\rm uf}^{(2)}, B_{\rm up}^{(2)}, B_{\rm pp}^{(2)}). \tag{2.67}$$

The right hand side of (2.67) is equal to

$$\begin{aligned} B_{\rm pf}^{(2)} = \;& (I-\Lambda)(A_{\rm up}^{(1)})^*\left(2H_0^{++}A_{\rm uf}^{(1)} - \epsilon_{\rm F}^0 A_{\rm uf}^{(1)} - A_{\rm uf}^{(1)}H_0^{--}\right) + \left[\mathcal{J}(A_W^{(1)})\right]_{\rm pf} \\ & +2A_{\rm pp}^{(1)}A_{\rm pf}^{(1)}(H_0^{--} - \epsilon_{\rm F}^0) + 2\Big[-(I-\Lambda)A_{\rm pf}^{(1)}W_{ff} - A_{\rm pp}^{(1)}W_{\rm pf} \\ & +\tfrac{1}{2}W_{\rm pp}(I-\Lambda)A_{\rm pf}^{(1)} + (I-\Lambda)(A_{\rm up}^{(1)})^*W_{\rm uf} + \tfrac{1}{2}(I-\Lambda)W_{\rm pp}A_{\rm pf}^{(1)} \\ & +(I-\Lambda)W_{\rm up}^*A_{\rm uf}^{(1)}\Big], \end{aligned}$$

$$
\begin{aligned}
B^{(2)}_{\rm uf} = \;& (2H_0^{++} - \epsilon^0_{\rm F})A^{(1)}_{\rm up}(I-\Lambda)A^{(1)}_{\rm pf} - A^{(1)}_{\rm up}(I-\Lambda)A^{(1)}_{\rm pf}H_0^{--} + \left[\mathcal{J}(A^{(1)}_W)\right]_{\rm uf} \\
& +2\left[-A^{(1)}_{\rm uf}W_{ff} - \tfrac{1}{2}A^{(1)}_{\rm up}(\Lambda+I)W_{\rm pf} + W_{\rm up}(I-\Lambda)A^{(1)}_{\rm pf} + W_{uu}A_{\rm uf}\right], \\
B^{(2)}_{\rm up} = \;& \left(2H_0^{++}A^{(1)}_{\rm uf} - \epsilon^0_{\rm F}A^{(1)}_{\rm uf} - A^{(1)}_{\rm uf}H_0^{--}\right)(A^{(1)}_{\rm pf})^*(I-\Lambda) + \left[\mathcal{J}(A^{(1)}_W)\right]_{\rm up} \\
& +2(H_0^{++} - \epsilon^0_{\rm F})A^{(1)}_{\rm up}A^{(1)}_{\rm pp} + \Big[-A_{\rm uf}W^*_{\rm pf}(\Lambda+I) - A^{(1)}_{\rm up}\Lambda W_{\rm pp} \\
& -A^{(1)}_{\rm up}W_{\rm pp}\Lambda + 2W_{\rm uf}(A^{(1)}_{\rm pf})^*(I-\Lambda) + 2W_{\rm up}M + 2W_{uu}A^{(1)}_{\rm up}\Lambda\Big], \\
B^{(2)}_{\rm pp} = \;& A^{(1)}_{\rm pf}(H_0^{--} - \epsilon^0_{\rm F})(A^{(1)}_{\rm pf})^* - (A^{(1)}_{\rm up})^*(H_0^{++} - \epsilon^0_{\rm F})A^{(1)}_{\rm up} + \left[\mathcal{J}(A^{(1)}_W)\right]_{\rm pp} \\
& +2\left[-A^{(1)}_{\rm pf}W^*_{\rm pf} + W^*_{\rm up}A^{(1)}_{\rm up}\right]
\end{aligned}
$$

while, $\mathcal{J}(A^{(1)}_W) = \left([\mathcal{J}(A^{(1)}_W)]_{\rm pf}, [\mathcal{J}(A^{(1)}_W)]_{\rm uf}, [\mathcal{J}(A^{(1)}_W)]_{\rm up}, [\mathcal{J}(A^{(1)}_W)]_{\rm pp}\right)$ is defined as follows: for any $A' \in \mathcal{A}$,

$$
\begin{aligned}
\langle \mathcal{J}(A^{(1)}_W); A'\rangle = 2\Big[& D\left(\rho_{\gamma_1(A')}, \rho_{\gamma_2(A^{(1)}_W, A^{(1)}_W)}\right) + D\left(\rho_{\gamma_1(A^{(1)}_W)}, \rho_{\gamma_2(A^{(1)}_W, A')}\right) \\
& + D\left(\rho_{\gamma_1(A^{(1)}_W)}, \rho_{\gamma_2(A', A^{(1)}_W)}\right)\Big].
\end{aligned}
$$

Chapter 3

Existence of optimal norm-conserving pseudopotentials for Kohn-Sham models

This chapter is concerned with the mathematical construction of pseudopotentials for electronic structure calculation. We first start by recalling the structure and the basis properties of the Kohn-Sham model for an atom, first with all-electron potentials, and second with norm-conserving pseudopotentials. The ground state mean-field Hamiltonian of an atom is rotation-invariant and its eigenfunctions therefore have specific properties, which we study in details since they play an important role in pseudopotential theory. The way of building norm-conserving pseudopotentials is described and the set of admissible semilocal norm-conserving pseudopotentials is defined. We prove that, for the Hartree (also called reduced Hartree-Fock) model, the latter set is nonempty and closed for an appropriate topology. We also prove some stability results of the Hartree model with pseudopotential, with respect to both external perturbations and variations of the pseudopotential itself. We then extend some of the results obtained in the framework of regular perturbation theory in Chapter 2 to the case of a perturbation by a uniform electric field (Stark potential). We construct in particular the first-order perturbation of the density matrix for both the all-electron and the pseudopotential Hartree model. We finally propose a new way to construct pseudopotentials consisting in choosing the "best" pseudopotential for some optimality criterion, and we prove the existence of an optimal pseudopotential for a variety of optimality criteria (some of them involving the linear response of the ground state atomic density to Stark potentials). Finally, we discuss possible extensions of our results to the Kohn-Sham LDA model. This work has been preprinted [25] and submitted for publication.

3.1 Introduction

It is a well-known theoretical and experimental fact that the core electrons of an atom are hardly affected by the chemical environment experienced by this atom. Pseudopotential methods are efficient model reduction techniques relying on this observation, which are widely used in electronic structure calculation, especially in solid state physics and materials science, as well as for the simulation of molecular systems containing heavy atoms. In pseudopotential methods, the original all-electron model is replaced by a reduced model explicitly dealing with valence electrons only, while core electrons are frozen in some reference state. The valence electrons are described by valence pseudo-orbitals, and the interaction between the valence electrons and the ionic cores (an ionic core consists of a nucleus and of the associated core electrons) is modeled by a nonlocal operator called a pseudopotential, constructed once and for all from single-atom reference calculations. The reduction of dimensionality obtained by eliminating the core electrons from the explicit calculation results in a much less computationally expensive approach. The pseudopotential has the property that, for isolated atoms, the valence pseudo-orbitals differ from the valence orbitals in the vicinity of the nucleus, *i.e.* in the so-called core region, but coincide with the valence orbitals out of the core region, *i.e.* in the region where the influence of the chemical environment is important. In addition to the reduction of dimensionality mentioned above, an advantage of pseudopotential models is that pseudopotentials are constructed in such a way that the valence pseudo-orbitals oscillate much less than the valence orbitals in the core region, hence can be approximated using smaller planewave bases, or discretized on coarser grids. In addition, pseudopotentials can be used to incorporate relativistic effects in non-relativistic calculations. This is of major interest for the simulation of heavy atoms with relativistic core electrons.

The concept of pseudopotential was first introduced by Hellmann [43] as early as in 1934. Several variants of the pseudopotential method were then developed over the years. Let us mention in particular Kerker's pseudopotentials [48], Troullier-Martins [87] and Kleinman-Bylander [49] norm-conserving pseudopotentials, Vanderbilt ultrasoft pseudopotentials [91], and Goedecker pseudopotentials [37]. Blochl's Projected Augmented Wave (PAW) method [10] can also be interpreted, to some extend, as a pseudopotential method. Although existing pseudopotential methods can be justified by convincing chemical arguments and work satisfactorily in practice, they are obtained by ad hoc procedures, so that the error introduced by the pseudopotential approximation is difficult to quantify *a priori*.

The purpose of this article is to clarify the mathematical framework underlying the construction of semilocal norm-conserving pseudopotentials for Kohn-Sham calculations, and to prove the existence of optimal pseudopotentials for a natural family of optimality criteria. We focus here on theoretical issues; the practical interest of this approach will be investigated in future works. In Section 3.2, we recall the mathematical structures of all-electron and norm-conserving pseudopotential Kohn-Sham models. In Section 3.3.2, we provide some results on the spectra of Hartree Hamiltonians for neutral atoms upon which the construction of pseudopotentials is based. Recall that the Hartree model is obtained from the exact Kohn-Sham model by discarding the exchange-correlation energy functional. We then define and analyze in Sections 3.3.3 to 3.3.5 the set of admissible semilocal norm-conserving pseudopotentials. After establishing in Section 3.3.6 some stability results of the Hartree ground state with respect to both external perturbations and small variations of

the pseudopotential, we propose in Section 3.3.7 a new way to construct pseudopotentials, consisting of choosing the best candidate in the set of all admissible pseudopotentials for a given optimality criterion. Most of our results are concerned with the Hartree model. Extensions to the LDA (local density approximation) model are discussed in Section 3.4. All the proofs are collected in Section 3.5.

3.2 Kohn-Sham models

Throughout this article, we use atomic units, in which $\hbar = 1$, $m_e = 1$, $e = 1$ and $4\pi\epsilon_0 = 1$, where $\hbar$ is the reduced Planck constant, m_e the electron mass, e the elementary charge, and ϵ_0 the dielectric permittivity of the vacuum. For simplicity, we only consider here restricted spin-collinear Kohn-Sham models (see [38] for a mathematical analysis of unrestricted and spin-noncollinear Kohn-Sham models) in which the diagonal components $\gamma^{\uparrow\uparrow}$ and $\gamma^{\downarrow\downarrow}$ of the spin-dependent density matrix are equal, and the off-diagonal components $\gamma^{\uparrow\downarrow}$ and $\gamma^{\downarrow\uparrow}$ are both equal to zero. A Kohn-Sham state can therefore be described by a density matrix

$$\gamma = \gamma^{\uparrow\uparrow} + \gamma^{\downarrow\downarrow} = 2\gamma^{\uparrow\uparrow} = 2\gamma^{\downarrow\downarrow}$$

satisfying the following properties:

- $\gamma \in \mathcal{S}(L^2(\mathbb{R}^3))$, where $\mathcal{S}(L^2(\mathbb{R}^3))$ denotes the space of the bounded self-adjoint operators on $L^2(\mathbb{R}^3)$;
- $0 \leq \gamma \leq 2$, which means $0 \leq (\phi, \gamma\phi)_{L^2} \leq 2\|\phi\|_{L^2}^2$ for all $\phi \in L^2(\mathbb{R}^3)$;
- $\mathrm{Tr}\,(\gamma)$ equals the number of electrons in the system.

As we do not consider here molecular models with magnetic fields, we can work in the space $L^2(\mathbb{R}^3)$ of *real-valued* square integrable functions on $\mathbb{R}^3$.

3.2.1 All electron Kohn-Sham models

Consider a molecular system with N electrons and K point-like nuclei of charges $Z = (z_1, \cdots, z_K) \in \mathbb{N}^K$, located at positions $\mathbf{R} = (\mathbf{R}_1, \cdots, \mathbf{R}_K) \in (\mathbb{R}^3)^K$. The Kohn-Sham ground state of the system is obtained by solving the minimization problem

$$I_{Z,\mathbf{R}} = \inf\left\{E_{Z,\mathbf{R}}(\gamma),\ \gamma \in \mathcal{K}_N\right\}, \tag{3.1}$$

where

$$E_{Z,\mathbf{R}}(\gamma) = \mathrm{Tr}\left(\left(-\frac{1}{2}\Delta - \sum_{k=1}^{K} z_k|\cdot - \mathbf{R}_k|^{-1}\right)\gamma\right) + \frac{1}{2}D\left(\rho_\gamma, \rho_\gamma\right) + E_{\mathrm{xc}}\left(\rho_\gamma\right), \tag{3.2}$$

and

$$\mathcal{K}_N := \left\{\gamma \in \mathcal{S}(L^2(\mathbb{R}^3)) \mid 0 \leq \gamma \leq 2,\ \mathrm{Tr}\,(\gamma) = N,\ \mathrm{Tr}\,(-\Delta\gamma) < \infty\right\},$$

where $\mathrm{Tr}\,(-\Delta\gamma) := \mathrm{Tr}\,(|\nabla|\gamma|\nabla|)$, with $|\nabla| := (-\Delta)^{1/2}$. Recall that any $\gamma \in \mathcal{K}_N$ has a density $\rho_\gamma \in L^1(\mathbb{R}^3)$, defined by

$$\forall W \in L^\infty(\mathbb{R}^3), \quad \mathrm{Tr}\,(\gamma W) = \int_{\mathbb{R}^3} \rho_\gamma W,$$

which satisfies $\rho_\gamma \geq 0$ in $\mathbb{R}^3$ and $\sqrt{\rho}_\gamma \in H^1(\mathbb{R}^3)$, so that $\rho_\gamma \in L^1(\mathbb{R}^3) \cap L^3(\mathbb{R}^3)$. In particular,

$$\mathrm{Tr}\left(\left(-\frac{1}{2}\Delta - \sum_{k=1}^{K} z_k|\cdot - \mathbf{R}_k|^{-1}\right)\gamma\right) = \frac{1}{2}\mathrm{Tr}\left(-\Delta\gamma\right) - \sum_{k=1}^{K} z_k \int_{\mathbb{R}^3} \frac{\rho_\gamma(\mathbf{r})}{|\mathbf{r}-\mathbf{R}_k|}\,d\mathbf{r},$$

where the second term of the right-hand side is well-defined by virtue of Hardy and Hoffmann-Ostenhof inequalities [44]

$$0 \leq \int_{\mathbb{R}^3} \frac{\rho_\gamma(\mathbf{r})}{|\mathbf{r}-\mathbf{R}_k|}\,d\mathbf{r} \leq 2N^{1/2}\|\nabla\sqrt{\rho}_\gamma\|_{L^2} \leq 2N^{1/2}\mathrm{Tr}\left(-\Delta\gamma\right)^{1/2} < \infty.$$

The bilinear form $D(\cdot,\cdot)$ in (3.2) is the Coulomb interaction defined for all $(f,g) \in L^{6/5}(\mathbb{R}^3) \times L^{6/5}(\mathbb{R}^3)$ by

$$D(f,g) = \int_{\mathbb{R}^3}\int_{\mathbb{R}^3} \frac{f(\mathbf{r})\,g(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\,d\mathbf{r}\,d\mathbf{r}'. \tag{3.3}$$

Lastly, the exchange-correlation energy functional E_{xc} depends on the Kohn-Sham model under consideration. We will restrict ourselves to two different Kohn-Sham models, namely the Hartree model, also called the reduced Hartree-Fock model, for which

$$E_{\mathrm{xc}}^{\mathrm{Hartree}}(\rho) = 0,$$

and the Kohn-Sham LDA (local density approximation) model [51], for which

$$E_{\mathrm{xc}}^{\mathrm{LDA}}(\rho) = \int_{\mathbb{R}^3} \epsilon_{\mathrm{xc}}(\rho(\mathbf{r}))\,d\mathbf{r},$$

where for each $\overline{\rho} \in \mathbb{R}_+$, $\epsilon_{\mathrm{xc}}(\overline{\rho}) \in \mathbb{R}_-$ is the exchange-correlation energy density of the homogeneous electron gas with uniform density $\overline{\rho}$. The function $\overline{\rho} \mapsto \epsilon_{\mathrm{xc}}(\overline{\rho})$ does not have a simple explicit expression, but it has the same mathematical properties as the exchange energy density of the homogeneous electron gas given by $\epsilon_{\mathrm{x}}(\overline{\rho}) = -\frac{3}{4}\left(\frac{3}{\pi}\right)^{1/3}\overline{\rho}^{4/3}$.

We are now going to recall some existence and uniqueness results for the Hartree model proved in [23, 81]. Although general results for neutral and positively charged molecular systems are available, we focus here on the case of a single neutral atom, which is of particular interest for the study of pseudopotentials. Weaker results have been obtained for the Kohn-Sham LDA model [4] (see also Section 3.4).

For convenience, we will call *atom z* the neutral atom with atomic number z.

Proposition 20 (All-electron Hartree model for neutral atoms [23, 81])**.** *Let $z \in \mathbb{N}^*$. The all-electron Hartree model for atom z*

$$I_z^{\mathrm{AA}} := \inf\left\{E_z^{\mathrm{AA}}(\gamma),\ \gamma \in \mathcal{K}_z\right\}, \tag{3.4}$$

where

$$E_z^{\mathrm{AA}}(\gamma) = \mathrm{Tr}\left(-\frac{1}{2}\Delta\gamma\right) - z\int_{\mathbb{R}^3}\frac{\rho_\gamma(\mathbf{r})}{|\mathbf{r}|}\,d\mathbf{r} + \frac{1}{2}D\left(\rho_\gamma,\rho_\gamma\right),$$

has a minimizer γ_z^0, and all the minimizers of (3.4) share the same density ρ_z^0. In addition,

1. *the ground state density ρ_z^0 is a radial positive function belonging to $H^2(\mathbb{R}^3) \cap C^{0,1}(\mathbb{R}^3) \cap C^\infty(\mathbb{R}^3 \setminus \{0\})$ (hence vanishing at infinity);*

2. *the Hartree Hamiltonian*

$$H_z^{\mathrm{AA}} = -\frac{1}{2}\Delta + W_z^{\mathrm{AA}}, \quad \textit{where} \quad W_z^{\mathrm{AA}} = -\frac{z}{|\cdot|} + \rho_z^0 \star |\cdot|^{-1}$$

is a bounded below self-adjoint operator on $L^2(\mathbb{R}^3)$ with domain $H^2(\mathbb{R}^3)$ and such that $\sigma_{\mathrm{ess}}(H_z^{\mathrm{AA}}) = [0, +\infty)$;

3. *the minimizers γ_z^0 satisfy the first-order optimality condition*

$$\gamma_z^0 = 2\mathbb{1}_{(-\infty, \epsilon_{z,\mathrm{F}}^0)}(H_z^{\mathrm{AA}}) + \delta,$$

where $\epsilon_{z,\mathrm{F}}^0 \leq 0$ is the Fermi level (that is the Lagrange multiplier of the constraint $\mathrm{Tr}\,(\gamma) = z$), and where δ is a finite-rank operator such that $0 \leq \delta \leq 2$ and $\mathrm{Ran}(\delta) \subset \mathrm{Ker}(H_z^{\mathrm{AA}} - \epsilon_{z,\mathrm{F}}^0)$;

4. *if $\epsilon_{z,\mathrm{F}}^0$ is negative and is not an accidentally degenerate eigenvalue of H_z^{AA}, then the minimizer γ_z^0 of (3.4) is unique.*

Remark 21 (on the Fermi level)**.** *Consider, for each $j \in \mathbb{N}^*$, the real number*

$$\varepsilon_{z,j} := \inf_{X_j \in \mathcal{X}_j} \sup_{\phi \in X_j \setminus \{0\}} \frac{\langle \phi | H_z^{\mathrm{AA}} | \phi \rangle}{\|\phi\|_{L^2}^2}, \tag{3.5}$$

where $\mathcal{X}_j$ is the set of the vector subspaces of $H^1(\mathbb{R}^3)$ of dimension j and $\langle \phi | H_z^{\mathrm{AA}} | \phi \rangle$ the quadratic form associated with the self-adjoint operator H_z^{AA} (whose form domain is $H^1(\mathbb{R}^3)$). According to the minmax principle [69, Theorem XIII.1], $\varepsilon_{z,j}$ is equal to the j^{th} lowest eigenvalue of H_z^{AA} (counting multiplicities) if H_z^{AA} has at least j non-positive eigenvalues (still counting multiplicities), and to $\min(\sigma_{\mathrm{ess}}(H_z^{\mathrm{AA}})) = 0$ otherwise. If z is odd, then $\epsilon_{z,\mathrm{F}}^0 = \varepsilon_{z,(z+1)/2}$. If z is even, that is if $z = 2N_{\mathrm{p}}$, where N_{p} is the number of electron pairs, two cases can be distinguished: if $\varepsilon_{z,N_{\mathrm{p}}} = \varepsilon_{z,N_{\mathrm{p}}+1}$, then $\epsilon_{z,\mathrm{F}}^0 = \varepsilon_{z,N_{\mathrm{p}}}$, otherwise, any number in the interval $(\varepsilon_{z,N_{\mathrm{p}}}, \varepsilon_{z,N_{\mathrm{p}}+1})$ is an admissible Lagrange multiplier of the constraint $\mathrm{Tr}\,(\gamma) = z$.

Remark 22 (on essential and accidental degeneracies)**.** *Let us clarify the meaning of the last statement of Proposition 20. The mean-field operator H_z^{AA} being invariant with respect to rotations, some of its eigenvalues may be degenerate. More precisely, all its eigenvalues corresponding to p, d, f, ... shells (see Section 3.3.2) are degenerate, and only those corresponding to s shells are (in general) non-degenerate. Eigenvalue degeneracies due to symmetries are called essential. By contrast, eigenvalues degeneracies of H_z^{AA} which are not due to rotational symmetry are called accidental. For instance, the fact that the 2s and 2p shells of the Hamiltonian $H = -\frac{1}{2}\Delta - \frac{1}{|\cdot|}$ (hydrogen atom) both correspond to the eigenvalue $-1/8$ is an accidental degeneracy. We have checked numerically that $\epsilon_{z,\mathrm{F}}^0$ is negative and is not an accidentally degenerate eigenvalue for any $1 \leq z \leq 20$. On the other hand, for $z = 21$, $\epsilon_{z,\mathrm{F}}^0$ is very close or equal to zero (see [24]).*

3.2.2 Kohn-Sham models with norm-conserving pseudopotentials

In pseudopotential calculations, the electrons of each chemical element are partitioned into two categories, core electrons on the one hand and valence electrons on the other hand, according to the procedure detailed in Section 3.3.4 below. We denote by $N_{z,\mathrm{c}}$ the number of core electrons in atom z, and by $N_{z,\mathrm{v}} = z - N_{z,\mathrm{c}}$ the number of valence electrons. Each chemical element is associated with a bounded nonlocal rotation-invariant self-adjoint operator V_z^{PP}, called the atomic pseudopotential, a core pseudo-density $\widetilde{\rho}^0_{z,\mathrm{c}} \in L^1(\mathbb{R}^3) \cap L^3(\mathbb{R}^3)$, and a core energy $E_{z,\mathrm{c}} \in \mathbb{R}$ which will be precisely defined in Section 3.3.5. Only valence electrons are explicitly dealt with in pseudopotential calculations. For the molecular system considered in Section 3.2.1, the pseudopotential approximation of the ground state energy is given by

$$I^{\mathrm{PP}}_{Z,\mathbf{R}} = \inf\left\{E^{\mathrm{PP}}_{Z,\mathbf{R}}(\widetilde{\gamma}),\ \widetilde{\gamma} \in \mathcal{K}_{N_{\mathrm{v}}}\right\} + \sum_{k=1}^{K} E_{z_k,\mathrm{c}}, \tag{3.6}$$

where

$$N_{\mathrm{v}} = N - \sum_{k=1}^{K} N_{z_k,\mathrm{c}}$$

is the total number of valence electrons in the system ($N_{\mathrm{v}} = \sum_{k=1}^{K} N_{z_k,v}$ if the system is electrically neutral). The Kohn-Sham pseudo-energy functional is

$$E^{\mathrm{PP}}_{Z,\mathbf{R}}(\widetilde{\gamma}) = \mathrm{Tr}\left(\left(-\frac{1}{2}\Delta + \sum_{k=1}^{K} \tau_{\mathbf{R}_k} V^{\mathrm{PP}}_{z_k} \tau_{-\mathbf{R}_k}\right)\widetilde{\gamma}\right) + \frac{1}{2}D\left(\rho_{\widetilde{\gamma}}, \rho_{\widetilde{\gamma}}\right) + E_{\mathrm{xc}}\left(\rho_{\widetilde{\gamma}} + \sum_{k=1}^{K} \tau_{\mathbf{R}_k}(\widetilde{\rho}^0_{z_k,\mathrm{c}})\right),$$

where for all $\mathbf{R} \in \mathbb{R}^3$, $\tau_{\mathbf{R}}$ is the translation operator defined on $L^2(\mathbb{R}^3)$ by $(\tau_{\mathbf{R}}\phi)(\mathbf{r}) = \phi(\mathbf{r} - \mathbf{R})$.

We will describe the precise nature of the atomic pseudopotentials V_z^{PP} in Section 3.3.5. Let us just mention at this stage that V_z^{PP} is a rotation-invariant operator of the form

$$V_z^{\mathrm{PP}} = V_{z,\mathrm{loc}} + \mathcal{V}_{z,\mathrm{nl}} \tag{3.7}$$

where $V_{z,\mathrm{loc}}$ and $\mathcal{V}_{z,\mathrm{nl}}$ are respectively the local and nonlocal parts of the pseudopotential operator V_z^{PP}. The operator $V_{z,\mathrm{loc}}$ is a multiplication operator by a real-valued radial function $V_{z,\mathrm{loc}} \in L^2_{\mathrm{loc}}(\mathbb{R}^3)$ satisfying

$$V_{z,\mathrm{loc}}(\mathbf{r}) \underset{|\mathbf{r}|\to\infty}{\sim} -\frac{N_{z,\mathrm{v}}}{|\mathbf{r}|}. \tag{3.8}$$

The operator $\mathcal{V}_{z,\mathrm{nl}}$ is a $-\Delta$-compact, rotation-invariant, bounded self-adjoint operator on $L^2(\mathbb{R}^3)$ such that

$$\forall \phi \in L^2(\mathbb{R}^3), \quad \left(\text{ess-Supp}(\phi) \subset \mathbb{R}^3 \setminus \overline{B}_{r_{\mathrm{c}}}\right) \quad \Rightarrow \quad \left(\mathcal{V}_{z,\mathrm{nl}}\phi = 0\right), \tag{3.9}$$

where r_{c} is a positive real number (depending of z) called the core radius of atom z, and where $\overline{B}_{r_{\mathrm{c}}}$ is the closed ball of $\mathbb{R}^3$ centered at the origin, with radius r_{c}.

The results below are straightforward extensions of the existence and uniqueness results established in [4, 23, 81]. We skip their proofs for brevity.

Proposition 23 (Kohn-Sham models with norm-conserving pseudopotential)**.** *Assume that the molecular system is neutral or positively charged, and that the atomic pseudopotentials satisfy (3.7)-(3.9). Then*

1. *the Hartree model (3.6) with $E_{\rm xc} = E_{\rm xc}^{\rm Hartree} = 0$ has a minimizer and all the minimizers share the same density;*
2. *the Kohn-Sham LDA model (3.6) with $E_{\rm xc} = E_{\rm xc}^{\rm LDA}$ has a minimizer.*

Proposition 24 (Hartree model for neutral atoms and norm-conserving pseudopotentials)**.** *Let $z \in \mathbb{N}^*$. If the atomic pseudopotential $V_z^{\rm PP}$ satisfies (3.7)-(3.9), then the Hartree model*

$$\inf\left\{E_z^{\rm PP}(\widetilde{\gamma}),\ \widetilde{\gamma} \in \mathcal{K}_{N_{z,\rm v}}\right\}, \tag{3.10}$$

where

$$E_z^{\rm PP}(\widetilde{\gamma}) = \mathrm{Tr}\left(\left(-\frac{1}{2}\Delta + V_z^{\rm PP}\right)\widetilde{\gamma}\right) + \frac{1}{2}D\left(\rho_{\widetilde{\gamma}}, \rho_{\widetilde{\gamma}}\right),$$

has a minimizer $\widetilde{\gamma}_z^0$ and all the minimizers share the same density $\widetilde{\rho}_z^0$. In addition,

1. *the pseudo-density $\widetilde{\rho}_z^0$ is a radial positive function belonging to $H^2(\mathbb{R}^3)$ (hence vanishing at infinity); ;*
2. *the Hartree pseudo-Hamiltonian*

$$H_z^{\rm PP} = -\frac{1}{2}\Delta + W_z^{\rm PP}, \quad \text{where} \quad W_z^{\rm PP} = V_z^{\rm PP} + \widetilde{\rho}_z^0 \star |\cdot|^{-1}, \tag{3.11}$$

   corresponding to the pseudopotential $V_z^{\rm PP}$, is a bounded below self-adjoint operator on $L^2(\mathbb{R}^3)$ with domain $H^2(\mathbb{R}^3)$ and such that $\sigma_{\rm ess}(H_z^{\rm PP}) = [0, +\infty)$;
3. *the minimizers $\widetilde{\gamma}_z^0$ satisfy the first-order optimality condition*

$$\widetilde{\gamma}_z^0 = 2\mathbb{1}_{(-\infty, \widetilde{\epsilon}_{z,\rm F}^0)}(H_z^{\rm PP}) + \widetilde{\delta},$$

   where $\widetilde{\epsilon}_{z,\rm F}^0 \leq 0$ the pseudo Fermi level (the Lagrange multiplier associated with the constraint $\mathrm{Tr}\left(\widetilde{\gamma}\right) = N_{z,\rm v}$), and where $\widetilde{\delta}$ is a finite-rank operator such that $0 \leq \widetilde{\delta} \leq 2$ and $\mathrm{Ran}(\widetilde{\delta}) \subset \mathrm{Ker}(H_z^{\rm PP} - \widetilde{\epsilon}_{z,\rm F}^0)$;
4. *if $\widetilde{\epsilon}_{z,\rm F}^0$ is negative and is not an accidentally degenerate eigenvalue of $H_z^{\rm PP}$, then the minimizer $\widetilde{\gamma}_z^0$ of (3.4) is unique.*

Remark 25. *We will see in Section 3.3.5 that, by construction, the Fermi level $\epsilon_{z,\rm F}^0$ and the pseudo Fermi level $\widetilde{\epsilon}_{z,\rm F}^0$ are actually equal, and that if $\epsilon_{z,\rm F}^0$ is negative and is not an accidentally degenerate eigenvalue of $H_z^{\rm AA}$, then $\widetilde{\epsilon}_{z,\rm F}^0$ is (obviously) negative and is not an accidentally degenerate eigenvalue of $H_z^{\rm PP}$.*

3.3 Analysis of norm-conserving semilocal pseudopotentials

In this section, we restrict ourselves to the Hartree model. Extensions to the Kohn-Sham LDA model are discussed in Section 3.4.

3.3.1 Atomic Hamiltonians and rotational invariance

In both all-electron and pseudopotential calculations, atomic Hartree Hamiltonians are self-adjoint operators on $L^2(\mathbb{R}^3)$ invariant with respect to rotations around the nucleus (assumed located at the origin). These operators are therefore block-diagonal in the decomposition of $L^2(\mathbb{R}^3)$ associated with the eigenspaces of the operator $\mathbf{L}^2$ (the square of the angular momentum operator $\mathbf{L} = \mathbf{r} \times \mathbf{p} = \mathbf{r} \times (-i\nabla)$). More precisely, the Hilbert space $L^2(\mathbb{R}^3)$ can be decomposed as the direct sum of the pairwise orthogonal subspaces $\mathcal{H}_l := \mathrm{Ker}(\mathbf{L}^2 - l(l+1))$:

$$L^2(\mathbb{R}^3) = \bigoplus_{l \in \mathbb{N}} \mathcal{H}_l. \tag{3.12}$$

It is convenient to introduce the spaces

$$L^2_{\mathrm{o}}(\mathbb{R}) = \left\{ f \in L^2(\mathbb{R}) \mid f(-r) = -f(r) \text{ a.e.} \right\}$$

(odd square integrable functions on $\mathbb{R}$) and

$$L^2_{\mathrm{r}}(\mathbb{R}^3) = \left\{ u \in L^2(\mathbb{R}^3) \mid u \text{ is radial} \right\}$$

(radial square integrable functions on $\mathbb{R}^3$). To any $u \in L^2_{\mathrm{r}}(\mathbb{R}^3)$ is associated a (unique) function $R_u \in L^2_{\mathrm{o}}(\mathbb{R})$ such that

$$u(\mathbf{r}) = \frac{R_u(|\mathbf{r}|)}{\sqrt{2\pi}|\mathbf{r}|} \quad \text{for a.e. } \mathbf{r} \in \mathbb{R}^3.$$

When there is no ambiguity, we will also denote by

$$u(r) = \frac{R_u(r)}{\sqrt{2\pi} r} \quad \text{for a.e. } r \in \mathbb{R}$$

($r \mapsto u(r)$ then is an even function of r, belonging to the weighted L^2 space $L^2\left(\mathbb{R}, r^2 dr\right)$). It is easily checked that the mapping

$$\mathcal{R} : L^2_{\mathrm{r}}(\mathbb{R}^3) \ni u \mapsto R_u \in L^2_{\mathrm{o}}(\mathbb{R})$$

is unitary. For $s \in \mathbb{R}$, we denote by

$$H^s_{\mathrm{r}}(\mathbb{R}^3) \quad \text{and} \quad H^s_{\mathrm{o}}(\mathbb{R})$$

the subspaces of the Sobolev spaces $H^s(\mathbb{R}^3)$ and $H^s(\mathbb{R})$ consisting of radial, and odd distributions respectively, and, for $s \in \mathbb{R}_+$, we denote by $H^s_{\mathrm{loc,r}}(\mathbb{R}^3)$ the space of radial locally H^s distributions in $\mathbb{R}^3$.

Lemma 26. *For all $s \in \mathbb{R}_+$ and all $u \in H^s_{\mathrm{r}}(\mathbb{R}^3)$, we have that $R_u \in H^s_{\mathrm{o}}(\mathbb{R})$. In addition, the mapping $H^s_{\mathrm{r}}(\mathbb{R}^3) \ni u \mapsto R_u \in H^s_{\mathrm{o}}(\mathbb{R})$ is unitary.*

Denoting by $P_l \in \mathcal{S}(L^2(\mathbb{R}^3))$ the orthogonal projector on $\mathcal{H}_l$, the spaces $\mathcal{H}_l = \mathrm{Ran}(P_l)$ are given by

$$\mathcal{H}_l = \left\{ v_l(\mathbf{r}) = \sum_{m=-l}^{l} \frac{\sqrt{2}\, v_{l,m}(|\mathbf{r}|)}{|\mathbf{r}|} \mathcal{Y}^m_l\left(\frac{\mathbf{r}}{|\mathbf{r}|}\right) \;\middle|\; v_{l,m} \in L^2_{\mathrm{o}}(\mathbb{R}),\ \forall -l \le m \le l \right\},$$

where $(\mathcal{Y}_l^m)_{l\geq 0,\,-l\leq m\leq l}$ are the real spherical harmonics [94], normalized in such a way that

$$\int_{\mathbb{S}^2} \mathcal{Y}_l^m \mathcal{Y}_{l'}^{m'} = \delta_{ll'}\delta_{mm'},$$

where $\mathbb{S}^2$ is the unit sphere of $\mathbb{R}^3$. Clearly,

$$\forall v_l \in \mathcal{H}_l, \quad \|v_l\|^2_{L^2(\mathbb{R}^3)} = \sum_{m=-l}^{l} \|v_{l,m}\|^2_{L^2(\mathbb{R})}.$$

We also have for all $s \in \mathbb{R}_+$,

$$H^s(\mathbb{R}^3) = \bigoplus_{l\in\mathbb{N}} \left(\mathcal{H}_l \cap H^s(\mathbb{R}^3)\right),$$

$$\mathcal{H}_l \cap H^s(\mathbb{R}^3) = \left\{ v_l(\mathbf{r}) = \sum_{m=-l}^{l} \frac{\sqrt{2}\, v_{l,m}(|\mathbf{r}|)}{|\mathbf{r}|} \mathcal{Y}_l^m\left(\frac{\mathbf{r}}{|\mathbf{r}|}\right) \;\middle|\; v_{l,m} \in H^s_{\mathrm{o}}(\mathbb{R}),\ \forall -l \leq m \leq l \right\},$$

$$\forall v_l \in \mathcal{H}_l \cap H^1(\mathbb{R}^3), \quad \|v_l\|^2_{H^1(\mathbb{R}^3)} = \sum_{m=-l}^{l} \|v_{l,m}\|^2_{H^1(\mathbb{R})} + l(l+1) \sum_{m=-l}^{l} \|r^{-1} v_{l,m}\|^2_{L^2(\mathbb{R})},$$

$$\forall v_l \in \mathcal{H}_l \cap H^2(\mathbb{R}^3), \quad \|v_l\|^2_{H^2(\mathbb{R}^3)} = \sum_{m=-l}^{l} \left\| -v''_{l,m} + l(l+1) r^{-2} v_{l,m} + v_{l,m} \right\|^2_{L^2(\mathbb{R})}.$$

By rotational invariance, any atomic Hamiltonian H_z is block-diagonal in the decomposition (3.12), which we write

$$H_z = \bigoplus_{l\in\mathbb{N}} H_{z,l}. \tag{3.13}$$

3.3.2 All-electron atomic Hartree Hamiltonians

All-electron atomic Hartree Hamiltonians are Schrödinger operators of the form

$$H_z^{\mathrm{AA}} = -\frac{1}{2}\Delta + W_z^{\mathrm{AA}}, \tag{3.14}$$

where W_z^{AA} is the multiplication operator by the radial function

$$W_z^{\mathrm{AA}}(\mathbf{r}) = -\frac{z}{|\mathbf{r}|} + \left(\rho_z^0 \star |\cdot|^{-1}\right)(\mathbf{r}),$$

ρ_z^0 being the radial all-electron atomic Hartree ground state density of atom z (see Proposition 20). The operator $H_{z,l}^{\mathrm{AA}}$ associated with the decomposition (3.13) is the self-adjoint operator on $\mathcal{H}_l$ with domain $\mathcal{H}_l \cap H^2(\mathbb{R}^3)$ defined for all $v_l \in \mathcal{H}_l \cap H^2(\mathbb{R}^3)$ by

$$(H_{z,l}^{\mathrm{AA}} v_l)(\mathbf{r}) = \sum_{m=-l}^{l} \frac{\sqrt{2}}{|\mathbf{r}|} \left(-\frac{1}{2} v''_{l,m}(|\mathbf{r}|) + \frac{l(l+1)}{2|\mathbf{r}|^2} v_{l,m}(|\mathbf{r}|) + W_z^{\mathrm{AA}}(|\mathbf{r}|) v_{l,m}(|\mathbf{r}|) \right) \mathcal{Y}_l^m\left(\frac{\mathbf{r}}{|\mathbf{r}|}\right).$$

This leads us to introduce, for each $l \in \mathbb{N}$, the radial Schrödinger equations

$$-\frac{1}{2}R''(r) + \frac{l(l+1)}{2r^2}R(r) + W_z^{\mathrm{AA}}(r)R(r) = \epsilon R(r), \quad R \in H^1_{\mathrm{o}}(\mathbb{R}), \quad \int_{\mathbb{R}} R^2 = 1. \tag{3.15}$$

Recall that, for convenience, we also denote by W_z^{AA} the even function from $\mathbb{R}$ to $\mathbb{R}$ such that for all $\mathbf{r} \in \mathbb{R}^3$, $W_z^{\mathrm{AA}}(\mathbf{r}) = W_z^{\mathrm{AA}}(|\mathbf{r}|)$.

The spectral properties of atomic Hartree Hamiltonians which will be useful to construct atomic pseudopotentials are collected in the following proposition.

Proposition 27 (spectrum of atomic Hartree Hamiltonians)**.** *Let $z \in \mathbb{N}^*$ for which $\epsilon^0_{z,\mathrm{F}} < 0$. The atomic Hartree Hamiltonian H_z^{AA} is a bounded below self-adjoint operator on $L^2(\mathbb{R}^3)$ with domain $H^2(\mathbb{R}^3)$, and it holds for any $l \in \mathbb{N}$, $\sigma_{\mathrm{ess}}(H^{\mathrm{AA}}_{z,l}) = \sigma_{\mathrm{ess}}(H_z^{\mathrm{AA}}) = [0, +\infty)$. In addition,*

1. *H_z^{AA} has no strictly positive eigenvalues and the set of its non-positive eigenvalues is the union of the non-positive eigenvalues of the operators $H^{\mathrm{AA}}_{z,l}$, which are obtained by solving the one-dimensional spectral problem (3.15);*

2. *for each $l \in \mathbb{N}$, the negative eigenvalues of (3.15), if any, are simple, and the eigenfunctions associated with the n^{th} eigenvalue have exactly $n-1$ nodes on $(0, +\infty)$;*

3. *for each $l \in \mathbb{N}$, (3.15) has at most a finite number $n_{z,l}$ of negative eigenvalues. The sequence $(n_{z,l})_{l\in\mathbb{N}}$ is non-increasing and $n_{z,l} = 0$ for l large enough. We denote by*

$$l_z^+ = \min\{l \in \mathbb{N} \mid n_{z,l+1} = 0\};$$

4. *denoting by $(\epsilon_{z,n,l})_{1\le n\le n_{z,l}}$ the negative eigenvalues of (3.15), ranked in increasing order, we have*

$$\forall 0 \le l_1 < l_2 \le l_z^+, \quad \forall n \le n_{z,l_2}, \quad \epsilon_{z,n,l_1} < \epsilon_{z,n,l_2}. \tag{3.16}$$

We denote by $R_{z,n,l}$ the L^2-normalized eigenfunction associated with the (simple) eigenvalue $\epsilon_{z,n,l}$ of (3.15) taking positive values for $r > 0$ large enough:

$$R_{z,n,l} \in H^1_{\mathrm{o}}(\mathbb{R}), \quad -\frac{1}{2}R''_{z,n,l}(r) + \frac{l(l+1)}{2r^2}R_{z,n,l}(r) + W_z^{\mathrm{AA}}(r)R_{z,n,l}(r) = \epsilon_{z,n,l}R_{z,n,l}(r),$$
$$\int_{\mathbb{R}} R^2_{z,n,l} = 1, \quad R_{z,n,l}(r) > 0 \quad \text{for } r \gg 1.$$

An orthonormal family of eigenfunctions of the negative part of the atomic Kohn-Sham Hamiltonian H_z^{AA} is thus given by

$$\phi^m_{z,n,l}(\mathbf{r}) = \frac{\sqrt{2}\, R_{z,n,l}(|\mathbf{r}|)}{|\mathbf{r}|}\mathcal{Y}^m_l\left(\frac{\mathbf{r}}{|\mathbf{r}|}\right), \quad 0 \le l \le l_z^+,\ 1 \le n \le n_{z,l},\ -l \le m \le l.$$

Note that $\phi^m_{z,n,l} \in \mathcal{H}_l \cap H^2(\mathbb{R}^3)$.

Remark 28. *The integers l and m are respectively called the azimuthal and magnetic quantum numbers. With the labeling of the eigenvalues of $H_z^{\rm AA}$ we have chosen, the so-called principal quantum number is equal to $(n+l)$. Thus, the 2p and 4d shells of atom z respectively correspond to the eigenvalues $\epsilon_{z,1,1}$ (first eigenvalue of $H_z^{\rm AA}|_{\mathcal{H}_1}$) and $\epsilon_{z,2,2}$ (second eigenvalue of $H_z^{\rm AA}|_{\mathcal{H}_2}$).*

The ground state density matrix γ_z^0 can be written as

$$\gamma_z^0 = \sum_{l=0}^{l_z^+} \sum_{n=1}^{n_{z,l}} \sum_{m=-l}^{l} p_{z,n,l} |\phi_{z,n,l}^m\rangle\langle\phi_{z,n,l}^m|, \tag{3.17}$$

where $0 \leq p_{z,n,l} \leq 2$ is the occupation number of the Kohn-Sham orbital $\phi_{z,n,l}^m$. Note that $p_{z,n,l}$ is independent of the magnetic quantum number m. The occupation numbers are such that

$$p_{z,n,l} = 2 \text{ if } \epsilon_{z,n,l} < \epsilon_{z,\rm F}^0, \quad 0 \leq p_{z,n,l} \leq 2 \text{ if } \epsilon_{z,n,l} = \epsilon_{z,\rm F}^0, \quad p_{z,n,l} = 0 \text{ if } \epsilon_{z,n,l} > \epsilon_{z,\rm F}^0, \tag{3.18}$$

and

$$\sum_{l=0}^{l_z^+} \sum_{n=1}^{n_{z,l}} (2l+1) p_{z,n,l} = z.$$

We call occupied l-shells of atom z the shells s ($l=0$), p ($l=1$), d ($l=2$), f ($l=3$), ... for which $n_{z,l} > 0$ and $p_{z,1,l} > 0$. In view of (3.16)-(3.18) if a shell l is occupied, then so are all the shells l' with $l' < l$. Denoting by

$$l_z^- = \max\left\{0 \leq l \leq l_z^+ \mid p_{z,1,l} > 0\right\},$$

we thus obtain that all the shells $l \leq l_z^-$ are occupied, and all the shells $l_z^- < l \leq l_z^+$ (if any, see Remark 29 below) are unoccupied.

It follows from (3.17)-(3.18) that if $\epsilon_{z,\rm F}^0$ is not an eigenvalue of $H_z^{\rm AA}$ (non-degenerate case in the terminology used in [23]), that is if the highest occupied shell is fully occupied, then the ground state density matrix is unique and is the orthogonal projector

$$\gamma_z^0 = 2 \sum_{n,l,m \,\mid\, \epsilon_{z,n,l} < \epsilon_{z,\rm F}^0} |\phi_{z,n,l}^m\rangle\langle\phi_{z,n,l}^m| \quad \text{(non-degenerate case)}.$$

We also know (see Proposition 20 and Remark 22) that if $\epsilon_{z,\rm F}^0$ is an eigenvalue ϵ_{z,n_0,l_0} of $H_z^{\rm AA}$ which is negative (degenerate case in the terminology used in [23]), and is not accidentally degenerate, then the ground state density matrix is still unique and is given by

$$\gamma_z^0 = 2 \sum_{n,l,m \,\mid\, \epsilon_{z,n,l} < \epsilon_{z,\rm F}^0} |\phi_{z,n,l}^m\rangle\langle\phi_{z,n,l}^m| + \frac{z - N_{\rm f}}{2l_0+1} \sum_{m=-l_0}^{l_0} |\phi_{z,n_0,l_0}^m\rangle\langle\phi_{z,n_0,l_0}^m| \quad \text{(degenerate case)},$$

where

$$N_{\rm f} = 2 \sum_{n,l \,\mid\, \epsilon_{z,n,l} < \epsilon_{z,\rm F}^0} (2l+1)$$

is the number of electrons in the fully occupied shells.

3.3.3 Atomic semilocal norm-conserving pseudopotentials

Atomic norm-conserving pseudopotentials are operators of the form

$$V_z^{\rm PP} = V_{z,\rm loc} + \sum_{l=0}^{l_z} P_l \mathcal{V}_{z,l} P_l, \qquad \text{for some } l_z^- \le l_z \le l_z^+, \tag{3.19}$$

where $V_{z,\rm loc} \in H^s_{\rm loc,r}(\mathbb{R}^3)$ and where we recall that $P_l \in \mathcal{B}(L^2(\mathbb{R}^3))$ is the orthogonal projector on the space $\mathcal{H}_l$. The first term in the right-hand side of (3.19) therefore is a local operator, while the second term is nonlocal. The structure of the operator $\mathcal{V}_{z,l}$ depends on the nature of the pseudopotential under consideration:

- in semilocal pseudopotentials, $\mathcal{V}_{z,l}$ is a multiplication operator by a function $V_{z,l} \in H^s_{\rm r}(\mathbb{R}^3)$; otherwise stated, $\mathcal{V}_{z,l}$ is a local operator on $\mathcal{H}_l$;
- in Kleinman-Bylander pseudopotentials, $\mathcal{V}_{z,l}$ is a finite-rank rotation-invariant operator.

We restrict our analysis to semilocal pseudopotentials. The overall regularity of the pseudopotential is governed by the parameter s. For each $0 \le l \le l_z$, the function $V_{z,l}$ is supported in a ball of radius $r_{{\rm c},l}$. The positive number

$$r_{\rm c} := \max_{0\le l\le l_z} r_{{\rm c},l}$$

is called the core radius.

The operators $H^{\rm PP}_{z,l}$ involved in the decomposition (3.13) of the atomic Hartree pseudo-Hamiltonian $H_z^{\rm PP}$ are then given by: for all $0 \le l \le l_z$,

$$(H^{\rm PP}_{z,l} v_l)(\mathbf{r}) = \sum_{m=-l}^{l} \frac{\sqrt{2}}{|\mathbf{r}|} \left(-\frac{1}{2} v''_{l,m}(|\mathbf{r}|) + \frac{l(l+1)}{2|\mathbf{r}|^2} v_{l,m}(|\mathbf{r}|) + (W_{z,\rm loc} + V_{z,l})(\mathbf{r}) v_{l,m}(|\mathbf{r}|) \right) \mathcal{Y}_l^m\left(\frac{\mathbf{r}}{|\mathbf{r}|}\right),$$

and for all $l > l_z$,

$$(H^{\rm PP}_{z,l} v_l)(\mathbf{r}) = \sum_{m=-l}^{l} \frac{\sqrt{2}}{|\mathbf{r}|} \left(-\frac{1}{2} v''_{l,m}(|\mathbf{r}|) + \frac{l(l+1)}{2|\mathbf{r}|^2} v_{l,m}(|\mathbf{r}|) + W_{z,\rm loc}(\mathbf{r}) v_{l,m}(|\mathbf{r}|) \right) \mathcal{Y}_l^m\left(\frac{\mathbf{r}}{|\mathbf{r}|}\right),$$

where

$$W_{z,\rm loc} = V_{z,\rm loc} + \widetilde{\rho}_z^0 \star |\cdot|^{-1},$$

$\widetilde{\rho}_z^0$ being the ground state pseudo-density defined in Proposition 24.

The mathematical construction of a semilocal pseudopotential for atom z goes as follows:

Step 1: choose an energy window $\Delta E = (E_-, E_+) \subset \mathbb{R}_-$, which, in particular, defines a partition between core and valence electrons;

Step 2: choose the core radius $r_{\rm c}$ and the Sobolev exponent s, and check that the so-obtained set $\mathcal{M}_{z,\Delta E,r_{\rm c},s}$ of admissible pseudopotentials (see Section 3.3.5) is non-empty;

Step 3: choose the "best" pseudopotential in the set $\mathcal{M}_{z,\Delta E,r_{\rm c},s}$.

Steps 1 and 2 are detailed in the next two sections. In Section 3.3.6, we investigate the stability of the atomic ground state of the pseudopotential model with respect to both external perturbations and variations of the pseudopotential itself. In Section 3.3.7, we address the existence of optimal pseudopotentials for a variety of optimality criteria.

3.3.4 Partition between core and valence electrons

As mentioned above, the first task to construct a pseudopotential is to partition the electrons into core and valence electrons. We assume here that $z \in \mathbb{N}^*$ is such that $\epsilon^0_{z,\rm F} < 0$. This partitioning is made through the choice of an energy window $\Delta E = (E_-, E_+)$, with $-\infty < E_- < E_+ < 0$, containing the Fermi level $\epsilon^0_{z,\rm F}$ (or *a* Fermi level in the case when the highest occupied energy level is fully occupied, see Remark 21) and such that there exists an integer l_z satisfying $l_z^- \le l_z \le l_z^+$ and

$$\forall l \le l_z, \quad \#\left(\{\epsilon_{z,n,l}\}_{n\in\mathbb{N}} \cap \Delta E\right) = \#\left(\{\epsilon_{z,n,l}\}_{n\in\mathbb{N}} \cap \overline{\Delta E}\right) = 1, \tag{3.20}$$

$$\forall l > l_z, \quad \#\left(\{\epsilon_{z,n,l}\}_{n\in\mathbb{N}} \cap \Delta E\right) = 0. \tag{3.21}$$

All the electrons occupying the shells such that $\epsilon_{z,n,l} < E_-$ are considered as core electrons. For each $l \le l_z$, we denote by $n^\star_{z,l}$, the unique non-negative integer such that $\epsilon_{z,n^\star_{z,l},l} \in \Delta E$. The set $\left\{\epsilon_{z,n^\star_{z,l},l}\right\}_{0\le l\le l_z}$ constitute the set of the valence energy levels, which can *a priori* be fully occupied ($E_- < \epsilon_{z,n^\star_{z,l},l} < \epsilon^0_{z,\rm F}$), partially occupied ($\epsilon_{z,n^\star_{z,l},l} = \epsilon^0_{z,\rm F}$) or unoccupied ($\epsilon^0_{z,\rm F} < \epsilon_{z,n^\star_{z,l},l} < E_+$).

Remark 29. *Let us emphasize that it is not clear a priori that one can find energy windows ΔE satisfying (3.20)-(3.21). Here again, we need to rely on numerical simulations to establish that our assumptions make sense and are satisfied in practice, at least for some atoms. In another contribution [24] more focused on numerical simulations, we show in particular that for most atoms of the first four rows of the periodic table, $\epsilon^0_{z,\rm F} < 0$ and energy windows ΔE satisfying (3.20)-(3.21) do exist. Besides, for most atoms of the first four rows, atomic Hartree Hamiltonians do not seem to have unoccupied energy levels with negative energies, so that for those atoms, $l_z^+ = l_z^-$ and therefore $l_z = l_z^- = l_z^+$. For instance, it can be checked numerically that the Hartree valence energy levels of the copper atom ($z = 29$) are such that*

$$l_z = 2, \quad n^\star_{z,0} = 4, \quad n^\star_{z,1} = 2, \quad n^\star_{z,2} = 1, \quad E_- < \epsilon_{z,2,1} < \epsilon_{z,4,0} < \epsilon^0_{z,\rm F} = \epsilon_{z,1,2} < E_+, \quad \textit{(for Cu).}$$

This is the situation depicted on Fig. 1. The core and valence configurations are respectively denoted by $1s^2\ 2s^2\ 2p^6\ 3s^2$ *and* $3p^6\ 4s^2\ 3d^9$ *in the chemistry literature. Let us observe that the valence configuration of Cu for the Hartree model differs from the one obtained from the N-body Schrödinger equation with infinitesimal Coulomb repulsion [35], that is* $3p^6\ 3d^{10}\ 4s^1$.

We therefore have

$$N_{z,\rm c} = \sum_{n,l\,|\,\epsilon_{z,n,l}\le E_-} (2l+1)p_{z,n,l} \qquad \text{and} \qquad N_{z,\rm v} = z - N_{z,\rm c},$$

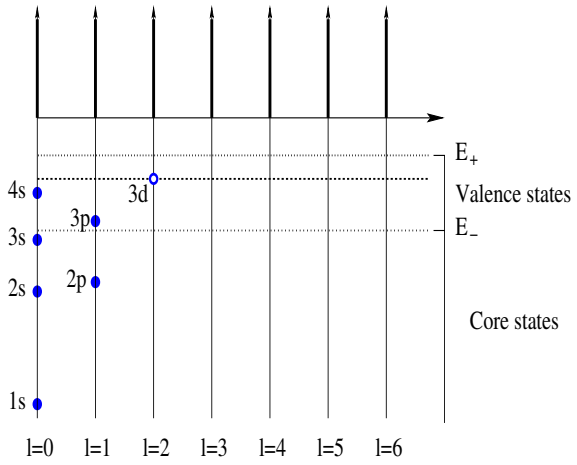


Figure 3.1 – Sketch of the spectra of the operators $H_z^{\mathrm{AA}}|_{\mathcal{H}_l}$ and admissible energy window $\Delta E = (E_-, E_+)$ for the copper atom ($z = 29$). The energy scale is arbitrary. The actual values of the energy levels are the following: $\epsilon_{z,1,0} \simeq -312.78$ Ha (1s), $\epsilon_{z,2,0} \simeq -36.42$ Ha (2s), $\epsilon_{z,1,1} \simeq -31.57$ Ha (2p), $\epsilon_{z,3,0} \simeq -3.716$ Ha (3s), $\epsilon_{z,2,1} \simeq -2.294$ Ha (3p), $\epsilon_{z,4,0} \simeq -5.540 \times 10^{-2}$ Ha (4s), $\epsilon^0_{z,\mathrm{F}} = \epsilon_{z,1,2} \simeq -1.371 \times 10^{-2}$ Ha (3d). The self-consistent Hartree Hamiltonian H_z^{AA} seems to have no negative eigenvalue above the Fermi level $\epsilon^0_{z,\mathrm{F}}$.

where we recall that $N_{z,\mathrm{c}}$ and $N_{z,\mathrm{v}}$ respectively denote the numbers of core and valence electrons. We also introduce the core and valence all-electron Hartree ground state densities, respectively defined as

$$\rho^0_{z,\mathrm{c}}(\mathbf{r}) := 2 \sum_{n,l \,|\, \epsilon_{z,n,l} \le E_-} \sum_{m=-l}^{l} |\phi^m_{z,n,l}(\mathbf{r})|^2 \quad \text{and} \quad \rho^0_{z,\mathrm{v}}(\mathbf{r}) := \sum_{l=0}^{l_z} \sum_{m=-l}^{l} p_{z,n^\star_{z,l},l} |\phi^m_{z,n^\star_{z,l},l}(\mathbf{r})|^2.$$

Note that the core density $\rho^0_{z,\mathrm{c}}$ should not be confused with the core pseudo-density $\widetilde{\rho}^0_{z,\mathrm{c}}$ mentioned in Section 3.2.2 and whose expression will be given below (see (3.32)).

3.3.5 Admissible pseudopotentials

Let $z \in \mathbb{N}^*$ be such that $\epsilon^0_{z,\mathrm{F}} < 0$, and let $\Delta E = (E_-, E_+)$ be an energy window satisfying the properties (3.20)-(3.21). An admissible semilocal norm-conserving pseudopotential with core radius r_{c} and regularity H^s ($s > 0$) is an operator V_z^{PP} of the form

$$V_z^{\mathrm{PP}} = V_{z,\mathrm{loc}} + \sum_{l=0}^{l_z} P_l V_{z,l} P_l, \qquad \text{for some } l_z^- \le l_z \le l_z^+,$$

for which the radial functions $V_{z,\mathrm{loc}}$ and $V_{z,l}$ satisfy the following properties:

1. **values out of the core region:**

$$\text{in } \mathbb{R}^3 \setminus B_{r_{\mathrm{c}}}, \quad V_{z,\mathrm{loc}} = -\frac{z}{|\cdot|} + \rho^0_{z,\mathrm{c}} \star |\cdot|^{-1} \quad \text{and} \quad V_{z,l} = 0 \text{ for all } 0 \le l \le l_z; \quad (3.22)$$

2. H^s**-regularity:**

$$V_{z,\mathrm{loc}} \in H^s_{\mathrm{loc,r}}(\mathbb{R}^3) \quad \text{and for all } 0 \le l \le l_z,\ V_{z,l} \in H^s_{\mathrm{r}}(\mathbb{R}^3); \tag{3.23}$$

3. **consistency:** the atomic Hartree pseudo-Hamiltonian

$$H_z^{\mathrm{PP}} = -\frac{1}{2}\Delta + W_z^{\mathrm{PP}}, \qquad \text{where} \qquad W_z^{\mathrm{PP}} = W_{z,\mathrm{loc}} + \sum_{l=0}^{l_z} P_l V_{z,l} P_l,$$

obtained with the pseudopotential V_z^{PP} (see Proposition 24) is such that

$$\mathbb{1}_{(-\infty,E_+)}(H_z^{\mathrm{PP}}) = \sum_{l=0}^{l_z} \sum_{m=-l}^{l} |\widetilde{\phi}^m_{z,l}\rangle\langle\widetilde{\phi}^m_{z,l}|, \tag{3.24}$$

$$W_{z,\mathrm{loc}} = V_{z,\mathrm{loc}} + \widetilde{\rho}_z^0 \star |\cdot|^{-1}, \qquad \widetilde{\rho}_z^0(\mathbf{r}) = \sum_{l=0}^{l_z} \sum_{m=-l}^{l} p_{z,n^\star_{z,l},l} |\widetilde{\phi}^m_{z,n^\star_{z,l},l}(\mathbf{r})|^2, \tag{3.25}$$

where

$$\widetilde{\phi}^m_{z,l}(\mathbf{r}) = \frac{\sqrt{2}\,\widetilde{R}_{z,l}(|\mathbf{r}|)}{|\mathbf{r}|} \mathcal{Y}^m_l\left(\frac{\mathbf{r}}{|\mathbf{r}|}\right), \tag{3.26}$$

with, for each $0 \le l \le l_z$,

$$\widetilde{R}_{z,l} \in H^1_{\mathrm{o}}(\mathbb{R}), \tag{3.27}$$

$$-\frac{1}{2}\widetilde{R}''_{z,l}(r) + \frac{l(l+1)}{2r^2}\widetilde{R}_{z,l}(r) + (W_{z,\mathrm{loc}}(r) + V_{z,l}(r))\,\widetilde{R}_{z,l}(r) = \epsilon_{z,n^\star_{z,l},l}\widetilde{R}_{z,l}(r), \tag{3.28}$$

$$\int_{\mathbb{R}} \widetilde{R}^2_{z,l} = 1, \tag{3.29}$$

$$\widetilde{R}_{z,l} = R_{z,n^\star_{z,l},l} \quad \text{on } (r_{\mathrm{c},l}, +\infty) \text{ for some } 0 < r_{\mathrm{c},l} \le r_{\mathrm{c}}, \tag{3.30}$$

$$\widetilde{R}_{z,l} \ge 0 \quad \text{on } (0, +\infty), . \tag{3.31}$$

We can therefore define the set of admissible semilocal norm-conserving pseudopotentials with energy window $\Delta E = (E_-, E_+)$, core radius r_{c} and regularity H^s, for the atom z as

$$\mathcal{M}_{z,\Delta E,r_{\mathrm{c}},s} := \left\{ V_z^{\mathrm{PP}} = V_{z,\mathrm{loc}} + \sum_{l=0}^{l_z} P_l V_{z,l} P_l \;\middle|\; \text{such that (3.22) – (3.31) hold} \right\}.$$

Several comments are in order:

- condition (3.22) implies conditions (3.8)-(3.9), so that the existence and uniqueness of the atomic ground state valence pseudo-density $\widetilde{\rho}_z^0$ is guaranteed by Proposition 24 as soon as (3.22) is satisfied;
- it follows from (3.27)-(3.29) and (3.31) that $\epsilon_{z,n^\star_{z,l},l}$ is the ground state eigenvalue of $H_z^{\mathrm{PP}}|_{\mathcal{H}_l}$ and that the $(2l+1)$ functions $\widetilde{\phi}^m_{z,l}$, $-l \le m \le l$, form an orthonormal basis of associated eigenfunctions;

- it also follows from (3.24) that the $\epsilon_{z,n^\star_{z,l},l}$'s are the only eigenvalues of $H_z^{\rm PP}$ in the energy range $(-\infty, E_+)$. This property is referred to as the *absence of ghost states* in the physics literature;

- out of the core region, (3.22) is compatible with (3.28) and (3.30). Indeed, (3.28) and (3.30) imply that

$$\forall \mathbf{r} \in \mathbb{R}^3 \setminus B_{r_{\rm c}}, \quad \widetilde{\rho}^0_z(\mathbf{r}) = \rho^0_{z,{\rm v}}(\mathbf{r}) \quad \text{and} \quad W_{z,{\rm loc}}(\mathbf{r}) + V_{z,l}(\mathbf{r}) = W_z^{\rm AA}(\mathbf{r}),$$

  hence, applying Gauss theorem, that $\widetilde{\rho}^0_z \star |\cdot|^{-1} = \rho^0_{z,{\rm v}} \star |\cdot|^{-1}$ in $\mathbb{R}^3 \setminus B_{r_{\rm c}}$, which finally leads to

$$V_{z,{\rm loc}} + V_{z,l} = W_z^{\rm AA} - \rho^0_{z,{\rm v}} \star |\cdot|^{-1} = -\frac{z}{|\cdot|} + \rho^0_{z,{\rm c}} \star |\cdot|^{-1} \quad \text{in } \mathbb{R}^3 \setminus B_{r_{\rm c}};$$

- the core energies and the core pseudo-densities $\widetilde{\rho}_{0,{\rm c}}$ of the atoms appearing in (3.6) are defined in such a way that for an isolated atom, the pseudopotential calculation gives the same energy as the all-electron model. In the Hartree case, the core energy of atom z is therefore given by

$$\begin{aligned} E_{z,{\rm c}} &= I_z^{\rm AA} - \inf\left\{E_z^{\rm PP}(\widetilde{\gamma}),\ \widetilde{\gamma} \in \mathcal{K}_{N_{z,{\rm v}}}\right\} \\ &= I_z^{\rm AA} - {\rm Tr}\left(\left(-\frac{1}{2}\Delta + V_z^{\rm PP}\right)\widetilde{\gamma}^0_z\right) - \frac{1}{2}D\left(\widetilde{\rho}^0_z, \widetilde{\rho}^0_z\right) \\ &= I_z^{\rm AA} - \sum_{l=0}^{l_z}(2l+1)p_{z,n^\star_{z,l},l}\epsilon_{z,n^\star_{z,l},l} + \frac{1}{2}D\left(\widetilde{\rho}^0_z, \widetilde{\rho}^0_z\right). \end{aligned}$$

  The core pseudo-density of atom z is defined by

$$\widetilde{\rho}^0_{z,{\rm c}} = \rho^0_z - \widetilde{\rho}^0_z. \tag{3.32}$$

  Note that atomic core pseudo-densities do not play any role in the Hartree model, since they are only involved in the exchange-correlation energy functional.

The rest of this section is devoted to the study of the set $\mathcal{M}_{z,\Delta E,r_{\rm c},s}$. We assume here that $z \in \mathbb{N}^*$ is such that $\epsilon^0_{z,{\rm F}} < 0$ and that $\Delta E = (E_-, E_+)$ is a fixed energy window satisfying (3.20)-(3.21). It readily follows from the definition of $\mathcal{M}_{z,\Delta E,r_{\rm c},s}$ that

$$\forall 0 < r_{\rm c} \le r'_{\rm c} < +\infty, \quad \mathcal{M}_{z,\Delta E,r_{\rm c},s} \subset \mathcal{M}_{z,\Delta E,r'_{\rm c},s}, \tag{3.33}$$

$$\forall 0 \le s \le s' < +\infty, \quad \mathcal{M}_{z,\Delta E,r_{\rm c},s'} \subset \mathcal{M}_{z,\Delta E,r_{\rm c},s}. \tag{3.34}$$

Let

$$r^-_{z,\Delta E,{\rm c}} = \max_{0 \le l \le l_z}\left(\max R^{-1}_{z,n^\star_{z,l},l}(0)\right) \ge 0$$

be the maximum over $0 \le l \le l_z$ of the largest node of the function $R_{z,n^\star_{z,l},l}$. If $r_{\rm c} < r^-_{z,\Delta E,{\rm c}}$, then (3.30) and (3.31) are obviously inconsistent, and $\mathcal{M}_{z,\Delta E,r_{\rm c},s} = \emptyset$. On the other hand, we are going to see that $\mathcal{M}_{z,\Delta E,r_{\rm c},s}$ is not empty, for any $s \ge 0$, as soon as $r_{\rm c}$ is large

enough. To any potential $W \in L^{3/2}_{\rm r}(\mathbb{R}^3)$, we associate the function $\mathcal{T}_W : (0,+\infty) \to \mathbb{R}_-$ defined for all $r > 0$ by

$$\mathcal{T}_W(r) := \inf_{\substack{\phi \in H^1_0(\Omega(r)) \\ \|\phi\|_{L^2(\Omega(r))} = 1}} \int_{\Omega(r)} \left(\frac{1}{2} |\nabla \phi|^2 + W \phi^2 \right),$$

where $\Omega(r) = \mathbb{R}^3 \setminus \overline{B}_r$. We will prove in Section 3.5.3 that $\mathcal{T}_{W_z^{\rm AA}}$ is continuous and non-decreasing, and that it maps $(0,+\infty)$ onto $(\varepsilon_{z,1}, 0]$ (where we recall that $\varepsilon_{z,1}$ is the lowest eigenvalue of $H_z^{\rm AA}$, see (3.5)).

Lemma 30. *Let $z \in \mathbb{N}^*$ be such that $\epsilon^0_{z,\rm F} < 0$. Let $\Delta E = (E_-, E_+)$ be an energy window satisfying (3.20)-(3.21). The equation $\mathcal{T}_{W_z^{\rm AA}}(r) = E_+$ has a unique solution $r^+_{z,\Delta E,\rm c} > 0$. In addition, $r^-_{z,\Delta E,\rm c} < r^+_{z,\Delta E,\rm c}$ and for all $r_{\rm c} \geq r^+_{z,\Delta E,\rm c}$ and all $s \geq 0$, the set $\mathcal{M}_{z,\Delta E,r_{\rm c},s}$ is nonempty.*

We were not able to provide a simple characterization of the critical core radius $r^0_{z,\Delta E,\rm c}$, $r^-_{z,\Delta E,\rm c} \leq r^0_{z,\Delta E,\rm c} \leq r^+_{z,\Delta E,\rm c}$, such that for all $s \geq 0$,

$$\forall r_{\rm c} < r^0_{z,\Delta E,\rm c}, \quad \mathcal{M}_{z,\Delta E,r_{\rm c},s} = \emptyset \quad \text{and} \quad \forall r_{\rm c} > r^0_{z,\Delta E,\rm c}, \quad \mathcal{M}_{z,\Delta E,r_{\rm c},s} \neq \emptyset.$$

We can only show, using the same regularization argument as in the proof of Lemma 30, that $r^0_{z,\Delta E,\rm c}$ is indeed independent of s.

Our next results will be established under the following:

Assumption 1: $z \in \mathbb{N}^*$ is such that $\epsilon^0_{z,\rm F}$ is negative and is not an accidentally degenerate eigenvalue of $H_z^{\rm AA}$, $\Delta E = (E_-, E_+)$ satisfies (3.20)-(3.21), $r_{\rm c} > r^0_{z,\Delta E,\rm c}$ and $s > 0$.

Consider now the Hilbert space

$$X_{z,\Delta E,r_{\rm c},s} = \left\{ v = v_{\rm loc} + \sum_{l=0}^{l_z} P_l v_l P_l \;\middle|\; (v_{\rm loc}, (v_l)_{0 \leq l \leq l_z}) \in (H^s_{0,\rm r}(B_{r_{\rm c}}))^{l_z+2} \right\} \;\equiv\; (H^s_{0,\rm r}(B_{r_{\rm c}}))^{l_z+2},$$

where $H^s_{0,\rm r}(B_{r_{\rm c}})$ is the closure in $H^s(\mathbb{R}^3)$ of the space of radial, real-valued, C^∞ functions on $\mathbb{R}^3$ with compact supports included in the open ball $B_{r_{\rm c}} := \left\{ \mathbf{r} \in \mathbb{R}^3 \,|\, |\mathbf{r}| < r_{\rm c} \right\}$, and the affine space

$$\mathcal{X}_{z,\Delta E,r_{\rm c},s} = \left\{ V = V_{\rm loc} + \sum_{l=0}^{l_z} P_l V_l P_l \;\middle|\; \text{such that (3.22)} - \text{(3.23) hold} \right\}.$$

Note that

$$\forall V \in \mathcal{X}_{z,\Delta E,r_{\rm c},s}, \quad \mathcal{X}_{z,\Delta E,r_{\rm c},s} = V + X_{z,\Delta E,r_{\rm c},s}.$$

As $\mathcal{M}_{z,\Delta E,r_{\rm c},s}$ is a subset of $\mathcal{X}_{z,\Delta E,r_{\rm c},s}$, we can endow the former set with the topology of the latter, and say that a sequence $(V^{\rm PP}_{z,k})_{k\in\mathbb{N}} \in \mathcal{M}_{z,\Delta E,r_{\rm c},s}$ of admissible pseudopotentials

- strongly converges to some $V \in \mathcal{X}_{z,\Delta E,r_{\rm c},s}$ if (with obvious notation)

$$\|V_{z,{\rm loc},k} - V_{\rm loc}\|^2_{H^s} + \sum_{l=0}^{l_z} \|V_{z,l,k} - V_l\|^2_{H^s} \underset{k\to\infty}{\to} 0; \tag{3.35}$$

- weakly converges to some $V \in \mathcal{X}_{z,\Delta E,r_{\rm c},s}$ if

$$\forall V' \in X_{z,\Delta E,r_{\rm c},s}, \quad \left(V_{z,{\rm loc},k} - V_{\rm loc}, V'_{\rm loc}\right)_{H^s} + \sum_{l=0}^{l_z} \left(V_{z,l,k} - V_l, V'_l\right)_{H^s} \underset{k\to\infty}{\to} 0. \quad (3.36)$$

Theorem 31 (properties of the set of norm-conserving pseudopotentials)**.** *Under Assumption 1, $\mathcal{M}_{z,\Delta E,r_{\rm c},s}$ is a nonempty weakly (hence strongly) closed subset of the affine space $\mathcal{X}_{z,\Delta E,r_{\rm c},s}$.*

In practice, pseudopotentials are constructed by first selecting optimal (for some criterion) pseudo-orbitals $\widetilde{R}_{z,l}$, $0 \le l \le l_z$, and then deducing from these functions the local and nonlocal components of the atomic pseudopotential using the relations

$$\forall \mathbf{r} \in \mathbb{R}^3 \setminus \{0\}, \quad V_{z,{\rm loc}}(\mathbf{r}) + V_{z,l}(\mathbf{r}) = \epsilon_{z,n^\star_{z,l},l} + \frac{1}{2}\frac{\widetilde{R}''_{z,l}(|\mathbf{r}|)}{\widetilde{R}_{z,l}(|\mathbf{r}|)} - \frac{l(l+1)}{2|\mathbf{r}|^2} - \left(\widetilde{\rho}^0_z \star |\cdot|^{-1}\right)(\mathbf{r}),$$

where $\widetilde{\rho}^0_z$ is defined by (3.26) and (3.25).

The following lemma is useful to select admissible functions $\widetilde{R}_{z,l}$.

Lemma 32. *Let $V_z^{\rm PP} \in \mathcal{M}_{z,\Delta E,r_{\rm c},s}$ for some $s > \frac{1}{2}$ (so that the functions $V_{z,{\rm loc}}$ and $V_{z,l}$ are continuous). For each $0 \le l \le l_z$, the radial function $\widetilde{R}_{z,l}$, defined by (3.27)-(3.31) in is $H^{s+2}_{\rm o}(\mathbb{R})$ and*

$$\widetilde{R}_{z,l}(r) = O(r^{l+1}) \quad as \quad r \to 0.$$

3.3.6 Some stability results

Let $z, \Delta E, r_{\rm c}, s$ satisfying Assumption 1. Let $V_z^{\rm PP} \in \mathcal{M}_{z,\Delta E,r_{\rm c},s}$ be a reference pseudopotential. It follows from Proposition 24 and the definition of $\mathcal{M}_{z,\Delta E,r_{\rm c},s}$ (see also Remark 25) that $\epsilon^0_{z,{\rm F}}$ is not an accidentally degenerate eigenvalue of $H_z^{\rm PP}$ and that the ground state pseudo-density matrix $\widetilde{\gamma}^0_z$ corresponding to $V_z^{\rm PP}$ is unique.

We can study the sensitivity of $\widetilde{\gamma}^0_z$ with respect to both an external perturbation and the choice of the pseudopotential by considering the minimization problem

$$\mathcal{E}_{V_z^{\rm PP}}(v, W) := \inf\left\{E_{V_z^{\rm PP}}(\widetilde{\gamma}, v, W),\ \widetilde{\gamma} \in \mathcal{K}_{N_{z,{\rm v}}}\right\}, \quad (3.37)$$

where the energy functional $E_{V_z^{\rm PP}}$ is defined on $\mathcal{K}_{N_{z,{\rm v}}} \times X_{z,\Delta E,r_{\rm c},s} \times \mathcal{C}'$ by

$$E_{V_z^{\rm PP}}(\widetilde{\gamma}, v, W) := {\rm Tr}\left(\left(-\frac{1}{2}\Delta + V_z^{\rm PP} + v\right)\widetilde{\gamma}\right) + \frac{1}{2}D(\rho_{\widetilde{\gamma}}, \rho_{\widetilde{\gamma}}) + \int_{\mathbb{R}^3} \rho_{\widetilde{\gamma}} W,$$

and where we have denoted by

$$\mathcal{C}' = \left\{W \in L^6(\mathbb{R}^3) \mid \nabla W \in (L^2(\mathbb{R}^3))^3\right\}$$

the space of potentials with finite Coulomb energies, endowed with the scalar product defined by

$$\forall (W_1, W_2) \in \mathcal{C}' \times \mathcal{C}', \quad (W_1, W_2)_{\mathcal{C}'} = \int_{\mathbb{R}^3} \nabla W_1 \cdot \nabla W_2.$$

For $\eta > 0$ and X a normed vector space, we denote by $B_\eta(X)$ the open ball of X with center 0 and radius η. The following result guarantees the stability of the pseudopotential model with respect to the choice of the pseudopotential.

Proposition 33. *Let $z, \Delta E, r_{\rm c}, s$ satisfying Assumption 1. Then, for all $V_z^{\rm PP} \in \mathcal{M}_{z,\Delta E,r_{\rm c},s}$, there exists $\eta > 0$ such that for all $(v, W) \in B_\eta(X_{z,\Delta E,r_{\rm c},s}) \times B_\eta(\mathcal{C}')$, problem (3.37) has a unique minimizer $\widetilde{\gamma}_{v,W}(V_z^{\rm PP})$. Moreover, for each $V_z^{\rm PP} \in \mathcal{M}_{z,\Delta E,r_{\rm c},s}$, the function $(v, W) \mapsto \widetilde{\gamma}_{v,W}(V_z^{\rm PP})$ is real analytic from $B_\eta(X_{z,\Delta E,r_{\rm c},s}) \times B_\eta(\mathcal{C}')$ to the space*

$$\mathfrak{S}_{1,1} := \left\{ T \in \mathfrak{S}_1(L^2(\mathbb{R}^3)) \cap \mathcal{S}(L^2(\mathbb{R}^3)) \mid |\nabla|T|\nabla| \in \mathfrak{S}_1(L^2(\mathbb{R}^3)) \right\},$$

$\mathfrak{S}_1(L^2(\mathbb{R}^3))$ denoting the space of the trace-class operators on $L^2(\mathbb{R}^3)$. For all $v \in X_{z,\Delta E,r_{\rm c},s}$, all $W \in \mathcal{C}'$, and all real numbers α and β such that $-\eta\|v\|^{-1}_{X_{z,\Delta E,r_{\rm c},s}} < \alpha < \eta\|v\|^{-1}_{X_{z,\Delta E,r_{\rm c},s}}$ and $-\eta\|W\|^{-1}_{\mathcal{C}'} < \beta < \eta\|W\|^{-1}_{\mathcal{C}'}$, we have

$$\widetilde{\gamma}_{\alpha v,\beta W}(V_z^{\rm PP}) = \widetilde{\gamma}_z^0 + \sum_{(j,k)\in(\mathbb{N}\times\mathbb{N})\setminus\{(0,0)\}} \alpha^j \beta^k \, \widetilde{\gamma}_{v,W}^{(j,k)}(V_z^{\rm PP}), \tag{3.38}$$

where $\widetilde{\gamma}_z^0$ is the ground state density matrix for the pseudopotential $V_z^{\rm PP}$, where the coefficients $\widetilde{\gamma}_{v,W}^{(j,k)}(V_z^{\rm PP})$ of the expansion are uniquely defined in $\mathfrak{S}_{1,1}$, and the series is normally convergent in $\mathfrak{S}_{1,1}$.

In the next section, we will define optimality criteria based on first-order perturbation method for choosing the "best" pseudopotential in the class $\mathcal{M}_{z,\Delta E,r_{\rm c},s}$. These criteria will involve the difference between the first-order response of the all-electron model and that of the pseudopotential model to a given external perturbation W. A natural external perturbation is the one obtained by subjecting the atom to an external uniform electric field (Stark effect):

$$W^{\rm Stark}(\mathbf{r}) = -\mathbf{r} \cdot \mathbf{e}, \tag{3.39}$$

where $\mathbf{e}$ is the unit vector of the vertical axis of the reference frame. As the unperturbed system is rotation-invariant, the direction of the electric field is unimportant. So is its magnitude since we only consider here first-order perturbations (linear responses).

Note that it is not possible to apply the results in Proposition 33 to the perturbation (3.39) since $W^{\rm Stark}$ is not in $\mathcal{C}'$. In the framework of the linear Schrödinger equation (see e.g. [69] for a detailed analysis of the case of the Hydrogen atom), the spectrum of a molecular Stark Hamiltonian is purely absolutely continuous and equal to $\mathbb{R}$ for all non-zero values of the electric field. The eigenstates of the unperturbed Hamiltonian turn into resonances. On the other hand, the perturbation series is well-defined; its convergence radius is equal to zero, but the energies and widths of the resonances can nonetheless be computed from the perturbation expansion using Borel summation techniques.

For the atomic Hartree model under consideration here, the perturbed energy functional has no minimizer: for all $\beta \neq 0$,

$$\inf\left\{E_z^{\rm AA}(\gamma) - \beta\int_{\mathbb{R}^3}\rho_\gamma(\mathbf{r}\cdot\mathbf{e}),\ \gamma\in\mathcal{K}_z\right\} = -\infty.$$

The same holds true for the corresponding pseudopotential model for any $V_z^{\rm PP} \in \mathcal{M}_{z,\Delta E,r_{\rm c},s}$. Physically, this corresponds to the fact that the infimum of the energy is obtained by allowing the electrons to go to infinity towards the regions where $W(\mathbf{r}) = -\beta\mathbf{r}\cdot\mathbf{e}$ goes to $-\infty$. As in the linear framework, each term of the perturbation series is well-defined, but the convergence radius of the series is equal to zero. We will only prove here the part of this result we need, namely that the first-order term of the perturbation expansion is well-defined, and, in the pseudopotential case, that the linear response is continuous with respect to the choice of the pseudopotential (see Theorem 34 below). We are not aware of an extension of the theory of resonances to nonlinear mean-field models of Kohn-Sham type.

For $V_z^{\rm PP} \in \mathcal{M}_{z,\Delta E,r_{\rm c},s}$ and $W \in \mathcal{C}'$, we denote by $\widetilde{\gamma}_W^{(k)}(V_z^{\rm PP}) := \widetilde{\gamma}_{0,W}^{(0,k)}(V_z^{\rm PP})$, where the right-hand side is defined in Proposition 33. We also denote by $\gamma_{z,W}^{(k)}$ the $k^{\rm th}$-order perturbation of the all-electron ground state γ_z^0 when atom z is subjected to an external potential $W \in \mathcal{C}'$. A consequence of [23, Theorems 5 and 12] and of the above Proposition 33 is that the linear maps

$$\mathcal{C}' \ni W \mapsto \gamma_{z,W}^{(1)} \in \mathfrak{S}_{1,1} \quad \text{and} \quad \mathcal{C}' \ni W \mapsto \widetilde{\gamma}_W^{(1)}(V_z^{\rm PP}) \in \mathfrak{S}_{1,1}, \quad V_z^{\rm PP} \in \mathcal{M}_{z,\Delta E,r_{\rm c},s}, \tag{3.40}$$

are continuous.

Theorem 34. *(Stark effect) Let $z, \Delta E, r_{\rm c}, s$ satisfying Assumption 1. The continuous linear maps defined by (3.40) can be extended in a unique way to continuous linear maps*

$$\mathcal{Y}_z \ni W \mapsto \gamma_W^{(1)} \in \mathfrak{S}_{1,1} \quad \textit{and} \quad \mathcal{Y}_z \ni W \mapsto \widetilde{\gamma}_W^{(1)}(V_z^{\rm PP}) \in \mathfrak{S}_{1,1}, \quad V_z^{\rm PP} \in \mathcal{M}_{z,\Delta E,r_{\rm c},s}, \tag{3.41}$$

where $\mathcal{Y}_z$ is the Banach space

$$\mathcal{Y}_z := \mathcal{C}' + L^2_{\rm w} \quad \textit{where} \quad L^2_{\rm w} := \left\{W \in L^2_{\rm loc}(\mathbb{R}^3) \mid \int_{\mathbb{R}^3} |W(\mathbf{r})|^2 e^{-\sqrt{|\epsilon^0_{z,\rm F}||\mathbf{r}|}}\, d\mathbf{r} < \infty\right\}.$$

In addition, $W^{\rm Stark} \in \mathcal{Y}_z$ and the mapping $\mathcal{M}_{z,\Delta E,r_{\rm c},s} \ni V_z^{\rm PP} \mapsto \widetilde{\gamma}^{(1)}_{W^{\rm Stark}}(V_z^{\rm PP}) \in \mathfrak{S}_{1,1}$ is compact.

3.3.7 Optimization of norm-conserving pseudopotentials

A natural way to choose a pseudopotential in the class $\mathcal{M}_{z,\Delta E,r_{\rm c},s}$ is to optimize some criterion $J(V_z^{\rm PP})$ combining the two requirements that the pseudopotential must be as smooth as possible and as transferable as possible. The smoothness requirement leads us to introduce the criterion

$$J_{\rm s}(V_z^{\rm PP}) := \frac{1}{2}\|W_z^{\rm PP}\|^2_{H^s} := \frac{1}{2}\left(\|W_{z,\rm loc}\|^2_{H^s} + \sum_{l=0}^{l_z}\|V_{z,l}\|^2_{H^s}\right), \tag{3.42}$$

where $W_z^{\rm PP}$ is the self-consistent pseudopotential corresponding to the pseudopotential $V_z^{\rm PP}$ (see Proposition 24). Note that it is natural to use the self-consistent pseudopotential $W_z^{\rm PP}$ rather than $V_z^{\rm PP}$ in the right-hand side of (3.42) since the smoothness of the Kohn-Sham pseudo-orbitals is controlled by $W_z^{\rm PP}$. Let us first state a general result.

Theorem 35. *Let $z, \Delta E, r_{\rm c}, s$ satisfying Assumption 1. Consider the criterion*

$$J(V_z^{\rm PP}) = \alpha J_{\rm s}(V_z^{\rm PP}) + J_{\rm t}(V_z^{\rm PP}),$$

where the smoothness criterion $J_{\rm s}$ is defined by (3.42), where the transferability criterion $J_{\rm t} : \mathcal{M}_{z,\Delta E,r_{\rm c},s} \to \mathbb{R}$ is a bounded below weakly lower-semicontinuous function, and where $\alpha > 0$ is a parameter allowing one to balance the smoothness and transferability requirements. Then, the optimization problem

$$\inf \left\{ J(V_z^{\rm PP}),\ V_z^{\rm PP} \in \mathcal{M}_{z,\Delta E,r_{\rm c},s} \right\} \tag{3.43}$$

has a minimizer.

Many different transferability criteria $J_{\rm t}$, based on various physical and chemical properties, can be considered. A natural choice is the criterion

$$J_{\rm t}^{\rm Stark}(V_z^{\rm PP}) := \frac{1}{2} \left\| \mathbb{1}_{\mathbb{R}^3 \setminus B_{r_{\rm c}}} \left(\widetilde{\rho}^{(1)}_{W^{\rm Stark}}(V_z^{\rm PP}) - \rho^{(1)}_{z,W^{\rm Stark}} \right) \right\|_{\mathcal{C}}^2, \tag{3.44}$$

where $\rho^{(1)}_{z,W^{\rm Stark}} = \rho_{\gamma^{(1)}_{z,W^{\rm Stark}}}$ and $\widetilde{\rho}^{(1)}_{W^{\rm Stark}}(V_z^{\rm PP}) = \rho_{\widetilde{\gamma}^{(1)}_{W^{\rm Stark}}(V_z^{\rm PP})}$ are respectively the first-order perturbations of the all-electron and pseudo densities of atom z, when the latter is submitted to the Stark potential (3.39). The Coulomb space $\mathcal{C}$ is defined as

$$\mathcal{C} = \left\{ \rho \in \mathcal{S}'(\mathbb{R}^3) \mid \widehat{\rho} \in L^1_{\rm loc}(\mathbb{R}^3),\ \|\rho\|_{\mathcal{C}}^2 := D(\rho,\rho) < \infty \right\},$$

where

$$D(f,g) := 4\pi \int_{\mathbb{R}^3} \frac{\overline{\widehat{f}(\mathbf{k})}\, \widehat{g}(\mathbf{k})}{|\mathbf{k}|^2}\, d\mathbf{k}. \tag{3.45}$$

Let us recall that $L^{6/5}(\mathbb{R}^3) \subset \mathcal{C}$, that the definitions (3.3) and (3.45) agree for $(f,g) \in L^{6/5}(\mathbb{R}^3) \times L^{6/5}(\mathbb{R}^3)$, and that $\mathcal{C}$ is therefore the space of all charge distributions ρ with finite Coulomb energy.

The following lemma shows that the transferability criterion $J_{\rm t}^{\rm Stark}$ is well-defined and falls into the scope of Theorem 35.

Lemma 36. *Let $z, \Delta E, r_{\rm c}, s$ satisfying Assumption 1. Then, $J_{\rm t}^{\rm Stark}$ is a well-defined bounded below weakly continuous mapping from $\mathcal{M}_{z,\Delta E,r_{\rm c},s}$ to $\mathbb{R}_+$.*

3.4 Extensions to the Kohn-Sham LDA model

It is probably quite difficult to extend to the LDA model the results established above for the Hartree model. As usual in the mathematical analysis of Kohn-Sham models, the main obstacle is that we do not know whether the atomic ground state density of atom

z is unique. We will therefore limit ourselves to comment on the extensions of our main results under some additional assumptions on the Kohn-Sham LDA ground state.

Assuming that the LDA ground state density ρ_z^0 of atom z is unique, hence radial, and that the LDA Fermi level of atom z is negative, it is then easy to show that the properties of the ground state density and of the atomic Hamiltonian listed in Propositions 1 and 8, as well as the result of uniqueness of the ground state density matrix, still hold for the all-electron Kohn-Sham LDA model. Likewise, the results in Proposition 5 are still valid for the LDA model under the assumption that the ground state pseudo-density $\widetilde{\rho}_z^0$ of atom z is unique. Note that the self-consistent potentials are then given, in the all-electron setting, by

$$W_z^{\mathrm{AA}} = -\frac{z}{|\cdot|} + \rho_z^0 \star |\cdot|^{-1} + v_{\mathrm{xc}}(\rho_z^0),$$

where $v_{\mathrm{xc}}(\rho_z^0) = \frac{d\epsilon_{\mathrm{xc}}}{d\rho}(\rho_z^0)$ is the exchange-correlation potential, and, in the pseudopotential setting, by

$$W_z^{\mathrm{PP}} = V_z^{\mathrm{PP}} + \widetilde{\rho_z^0} \star |\cdot|^{-1} + v_{\mathrm{xc}}(\widetilde{\rho}_{z,\mathrm{c}}^0 + \widetilde{\rho}_z^0).$$

Still under the above assumptions, Lemma 30 (nonemptyness of the set $\mathcal{M}_{z,\Delta E,r_{\mathrm{c}},s}$ of admissible pseudopotentials), Theorem 31 ($\mathcal{M}_{z,\Delta E,r_{\mathrm{c}},s}$ is a weakly closed subset of the affine space $\mathcal{X}_{z,\Delta E,r_{\mathrm{c}},s}$), and Theorem 35 (existence of an optimal pseudopotential in an abstract framework) can all be extended to the LDA setting.

Note that, in practice, the calibration of pseudopotentials is made under the assumption that the LDA ground state density (with or without pseudopotential) is radial. The calculations then boil down to solving coupled systems of radial Schrödinger equations (see [24, 49, 87] for details). To the best of our knowledge, no numerical evidence that the radial LDA ground state of an atom might not be unique has been published so far.

The extensions of our results involving nonlinear perturbation theory (Proposition 14, Theorem 15, and Lemma 17) require, on top of the above assumptions, an additional assumption on the uniform coercivity of the Hessian of the energy functional at the unperturbed local minimizer. As the exchange-correlation energy density is not twice differentiable at 0 (it behaves as the function $\mathbb{R}_+ \ni \rho \mapsto -\rho^{4/3} \in \mathbb{R}_-$), it is not clear that such an assumption is satisfied. As already mentioned in [23, Section 5], this technical problem is not encountered in Kohn-Sham calculations with periodic boundary conditions due to the fact that the ground state density then is both bounded and bounded away from zero.

3.5 Proofs

3.5.1 Proof of Lemma 26

The three-dimensional Fourier transform of a radial function $u \in L^2_{\mathrm{r}}(\mathbb{R}^3)$ is related to the one-dimensional Fourier transform of the function $R_u = \mathcal{R}(u)$ by the simple relation

$$\mathcal{F}_3(u)(\mathbf{k}) = \frac{i}{\sqrt{2\pi}|\mathbf{k}|}\mathcal{F}_1(R_u)(|\mathbf{k}|).$$

The above expression is a special case of the Grafakos-Teschl recursion formula [41]. We therefore have

$$\|u\|^2_{H^s(\mathbb{R}^3)} = \int_{\mathbb{R}^3} (1+|\mathbf{k}|^2)^s |\mathcal{F}_3(u)(\mathbf{k})|^2 \, d\mathbf{k} = \frac{1}{2\pi} \int_{\mathbb{R}^3} \frac{(1+|\mathbf{k}|^2)^s}{|\mathbf{k}|^2} |\mathcal{F}_1(R_u)(|\mathbf{k}|)|^2 \, d\mathbf{k}$$

$$= 2\int_0^\infty (1+k^2)^s |\mathcal{F}_1(R_u)(k)|^2 \, dk = \int_{-\infty}^{+\infty} (1+k^2)^s |\mathcal{F}_1(R_u)(k)|^2 \, dk = \|R_u\|^2_{H^s(\mathbb{R})}.$$

3.5.2 Proof of Proposition 27

The proof of Proposition 27 is based on the following observation.

Lemma 37. *Let $z \in \mathbb{N}^*$ such that $\epsilon^0_{z,\mathrm{F}} < 0$. The Hartree potential W^{AA}_z is a radial increasing negative function of $L^2_{\mathrm{r}}(\mathbb{R}^3) \cap C^\infty(\mathbb{R}^3 \setminus \{0\})$ converging exponentially fast to 0.*

Proof. The Hartree potential W^{AA}_z satisfies $-\Delta W^{\mathrm{AA}}_z = 4\pi(\rho^0_z - z\delta_0)$, where the ground state density ρ^0_z is in $\mathcal{C}$ and satisfies $\int_{\mathbb{R}^3} \rho^0_z = z$. We also know from Proposition 20 that ρ^0_z is a radial positive function belonging to $C^\infty(\mathbb{R}^3 \setminus \{0\})$. Therefore, W^{AA}_z is radial and belongs to $C^\infty(\mathbb{R}^3 \setminus \{0\})$, and we infer from Gauss theorem that for all $r > 0$,

$$4\pi r^2 \frac{dW^{\mathrm{AA}}_z}{dr}(r) = -4\pi \left(-z + \int_{B_r} \rho^0_z \right) = 4\pi \int_{\mathbb{R}^3 \setminus B_r} \rho^0_z > 0,$$

where B_r is the ball of $\mathbb{R}^3$ with center 0 and radius r. Hence, W^{AA}_z is a radial increasing function. Its limit at infinity is necessarily equal to zero since $W^{\mathrm{AA}}_z = -\frac{z}{|\cdot|} + \rho^0_z \star |\cdot|^{-1}$ with $\rho^0_z \star |\cdot|^{-1} \in \mathcal{C}' \subset L^6(\mathbb{R}^3)$. As $\epsilon^0_{z,\mathrm{F}} < 0$, the ground state density of the atom z is of the form

$$\rho^0_z(\mathbf{r}) = \sum_{i=1}^n p_i |\phi_i(\mathbf{r})|^2,$$

where the occupation numbers p_i are such that $0 \le p_i \le 2$ and $\sum_{i=1}^n p_i = z$, and where the orbitals ϕ_i satisfy

$$\phi_i \in H^2(\mathbb{R}^3), \quad -\frac{1}{2}\Delta\phi_i + W^{\mathrm{AA}}_z \phi_i = \epsilon_i \phi_i, \quad \int_{\mathbb{R}^3} \phi_i \phi_j = \delta_{ij}.$$

As $\epsilon_i \le \epsilon^0_{z,\mathrm{F}} < 0$ and W^{AA}_z goes to zero at infinity, we deduce from the maximum principle for second-order elliptic equations (see e.g. [36]) that for each $1 \le i \le n$, $\phi_i \, e^{\sqrt{|\epsilon^0_{z,\mathrm{F}}|}|\cdot|/2} \in L^\infty(\mathbb{R}^3)$. Therefore, there exists $C_z \in \mathbb{R}_+$ such that

$$\forall \mathbf{r} \in \mathbb{R}^3, \quad 0 < \rho^0_z(\mathbf{r}) \le C_z \, e^{-\sqrt{|\epsilon^0_{z,\mathrm{F}}|}|\mathbf{r}|}. \tag{3.46}$$

Hence,

$$\forall r > 0, \quad 0 \le \frac{dW^{\mathrm{AA}}_z}{dr}(r) = \frac{1}{r^2} \int_{\mathbb{R}^3 \setminus B_r} \rho^0_z \le \frac{C_z}{r^2} \int_{\mathbb{R}^3 \setminus B_r} e^{-\sqrt{|\epsilon^0_{z,\mathrm{F}}|}|\mathbf{r}'|} \, d\mathbf{r}'.$$

Integrating the above inequality leads to

$$\forall r \geq \frac{2}{\sqrt{|\epsilon^0_{z,\mathrm{F}}|}}, \quad 0 \geq W_z^{\mathrm{AA}}(r) \geq -\frac{4\pi r^2 C_z}{\sqrt{|\epsilon^0_{z,\mathrm{F}}|}}\, e^{-\sqrt{|\epsilon^0_{z,\mathrm{F}}|}r}.$$

Together with the fact that $W_z^{\mathrm{AA}} = -\frac{z}{|\cdot|} + \rho_z^0 \star |\cdot|^{-1} \in L^2_{\mathrm{loc}}(\mathbb{R}^3)$, this bound implies that $W_z^{\mathrm{AA}} \in L^2_{\mathrm{r}}(\mathbb{R}^3)$. □

The proof of Proposition 27 then follows from classical results on the spectra of rotation-invariant Schrödinger operators (see e.g. [69]), which we recall here for completeness. First, as the function W_z^{AA} is in $L^2_{\mathrm{r}}(\mathbb{R}^3)$, the operator $W_z^{\mathrm{AA}}(1-\Delta)^{-1}|_{\mathcal{H}_l} = (W_z^{\mathrm{AA}}(1-\Delta)^{-1})|_{\mathcal{H}_l}$ is Hilbert-Schmidt for each $l \in \mathbb{N}$ by the Kato-Seiler-Simon inequality [77] and the continuity of P_l. Therefore, W_z^{AA} is a compact perturbation of the operator $-\frac{1}{2}\Delta|_{\mathcal{H}_l}$, and we deduce from Weyl's theorem that $\sigma_{\mathrm{ess}}(H_{z,l}^{\mathrm{AA}}) = \sigma_{\mathrm{ess}}(-\frac{1}{2}\Delta|_{\mathcal{H}_l}) = [0, +\infty)$.

The absence of strictly positive eigenvalues of H_z^{AA} is a consequence of Lemma 37 and [69, Theorem XIII.56]. The set of the negative eigenvalues of H_z^{AA} is the union of the sets of the negative eigenvalues of (3.15) for $l \in \mathbb{N}$; this is a straightforward consequence of the decomposition (3.13).

The fact that for each $l \in \mathbb{N}$, the negative eigenvalues of (3.15), if any, are simple and that the eigenfunctions associated with the n^{th} eigenvalue have exactly $n-1$ nodes on $(0, +\infty)$ is a standard result on one-dimensional Schrödinger equations (Sturm's oscillation theory), which can be read in [27, 46] for instance.

Lemma 37, together with [69, Theorem XIII.9], implies that for each $l \in \mathbb{N}$, (3.15) has at most $(2l+1)^{-1}\int_0^{+\infty} r|W_z^{\mathrm{AA}}(r)|\,dr < \infty$ negative eigenvalues. Since this number is lower than 1 for l large enough, $H_{z,l}^{\mathrm{AA}}$ has no negative eigenvalue for l large enough. The monotonicity of the sequence $(n_{z,l})_{l\in\mathbb{N}}$ readily follows from the minmax principle. So does the last assertion.

3.5.3 Proof of Lemma 30

Let us first establish a couple of intermediate results.

Lemma 38. *Let $W \in L^{3/2}_{\mathrm{r}}(\mathbb{R}^3) \cap C^0(\mathbb{R}^3 \setminus \{0\})$. We denote by $\Omega(r) = \mathbb{R}^3 \setminus \overline{B}_r$, by $T_{W,r}$ the self-adjoint operator on $L^2(\Omega(r))$ with domain $H^1_0(\Omega(r)) \cap H^2(\Omega(r))$ defined by $T_{W,r}\phi = -\frac{1}{2}\Delta\phi + W\phi$ for all $\phi \in H^1_0(\Omega(r)) \cap H^2(\Omega(r))$, and by*

$$\mathcal{T}_W(r) := \min\left(\sigma(T_{W,r})\right) = \inf_{\substack{\phi \in H^1_0(\Omega(r)) \\ \|\phi\|_{L^2(\Omega(r))} = 1}} \int_{\Omega(r)} \left(\frac{1}{2}|\nabla\phi|^2 + W\phi^2\right).$$

We also introduce the self-adjoint operator $T_{W,0}$ on $L^2(\mathbb{R}^3)$ with domain $H^2(\mathbb{R}^3)$ defined by $T_{W,0}\phi = -\frac{1}{2}\Delta\phi + W\phi$ for all $\phi \in H^2(\mathbb{R}^3)$. Then, two situations may occur:

- *either $\min\left(\sigma(T_{W,0})\right) = 0$, in which case the function $\mathcal{T}_W$ is identically equal to zero on $(0, +\infty)$;*

- *or* $\min\left(\sigma(T_{W,0})\right) < 0$*, in which case there exists* $\widetilde{r}_{\mathrm{c}} \in (0,+\infty)$ *such that the function* $\mathcal{T}_W$ *is differentiable, strictly increasing and bijective from* $(0,\widetilde{r}_{\mathrm{c}})$ *to* $\left(\min\left(\sigma(T_{W,0})\right),0\right)$*, and identically equal to zero on* $(\widetilde{r}_{\mathrm{c}},+\infty)$*.*

Proof. Let $W \in L^{3/2}_{\mathrm{r}}(\mathbb{R}^3) \cap C^0(\mathbb{R}^3 \setminus \{0\})$. Since for any $0 < r < r' < \infty$, we have $\Omega(r') \subset \Omega(r)$, the function $\mathcal{T}_W$ is non-decreasing on $(0,+\infty)$. As $\sigma_{\mathrm{ess}}(T_{W,r}) = [0,+\infty)$, we have for all $0 < r < \infty$,

$$0 \geq \mathcal{T}_W(r) \geq \inf_{\phi \in H^1(\mathbb{R}^3) \,|\, \|\phi\|_{L^2}=1} \int_{\mathbb{R}^3} \left(\frac{1}{2}|\nabla\phi|^2 + \mathbb{1}_{\Omega(r)} W |\phi|^2 \right),$$

and it follows from [69, Theorem XIII.9] that the right-hand side is equal to zero for r large enough.

It also holds that $\sigma_{\mathrm{ess}}(T_{W,0}) = [0,+\infty)$. If $T_{W,0}$ has no negative eigenvalue, then the function $\mathcal{T}_W$ is identically equal to zero by the minmax principle. Otherwise, denoting by ϵ_1 the lowest negative eigenvalue of $T_{W,0}$, we have

$$\lim_{r \to 0} \mathcal{T}_W(r) = \epsilon_1.$$

This follows from the fact that $C^\infty_{\mathrm{c}}(\mathbb{R}^3 \setminus \{0\})$ is dense in $H^1(\mathbb{R}^3)$.

Lastly, for any $r \in (0,+\infty)$ such that $\mathcal{T}_W(r) < 0$, the operator $T_{W,r}$ has a negative non-degenerate ground state eigenvalue and a radial ground state $\phi_{W,r} \in H^1_0(\Omega(r)) \cap H^2(\Omega(r))$ such that $\|\phi_{W,r}\|_{L^2(\Omega(B_r))} = 1$ and $\phi_{W,r} > 0$ in $\Omega(r)$. By the Hopf's maximum principle for second-order linear elliptic equations [36], $\frac{\partial \phi_{W,r}}{\partial r} > 0$ on $\partial\Omega(r) = \partial B_r$. It is then well-known [80] that $\mathcal{T}_W$ is differentiable at r and that

$$\mathcal{T}'_W(r) = -\int_{\partial\Omega(r)} \frac{\partial \phi_{W,r}}{\partial n} = \int_{\partial B_r} \frac{\partial \phi_{W,r}}{\partial r} > 0.$$

Therefore, if $T_{W,0}$ has a negative eigenvalue, then the function $\mathcal{T}_W$ is continuous, there exists $0 < \widetilde{r}_{\mathrm{c}} < +\infty$ such that $\mathcal{T}_W$ is differentiable and strictly increasing on $(0,\widetilde{r}_{\mathrm{c}})$, and identically equal to zero on $[\widetilde{r}_{\mathrm{c}},+\infty)$, and $\mathcal{T}_W$ maps $(0,+\infty)$ onto $(\epsilon_1,0)$. □

It follows in particular from Lemma 38 that, since $W^{\mathrm{AA}}_z \in L^{3/2}_{\mathrm{r}}(\mathbb{R}^3) \cap C^0(\mathbb{R}^3 \setminus \{0\})$ by Lemma 37, and $\min(\sigma(H^{\mathrm{AA}}_z)) < E_+ < 0$, the equation $\mathcal{T}_{W^{\mathrm{AA}}_z}(r) = E_+$ has a unique solution $r^+_{z,\Delta E,\mathrm{c}}$.

The second intermediate result we need is the following.

Lemma 39. *Let* $l \in \mathbb{N}$*,* $s \in \mathbb{R}_+$*,* $E_+ < 0$ *and* $W \in L^{3/2}_{\mathrm{r}}(\mathbb{R}^3)$ *vanishing at infinity and such that* $W \in H^s(\Omega(\varepsilon))$*, for any* $\varepsilon > 0$*. Let* $R_l \in H^2_{\mathrm{o}}(\mathbb{R})$ *and* $\epsilon_l < E_+$ *be such that*

$$-\frac{1}{2}R''_l(r) + \frac{l(l+1)}{2r^2}R_l(r) + W(r)R_l(r) = \epsilon_l R_l(r), \quad \int_{\mathbb{R}} R_l^2 = 1.$$

Let r^+_{c} *be the unique positive real number such that* $\mathcal{T}_W(r^+_{\mathrm{c}}) = E_+$*. Then, for all* $r_{\mathrm{c}} > r^+_{\mathrm{c}}$*,*

there exists $\widetilde{W} \in H^s_{\mathrm{r}}(\mathbb{R}^3)$ *such that*

$$\widetilde{R}_l \in H^1_{\mathrm{o}}(\mathbb{R}), \tag{3.47}$$

$$-\frac{1}{2}\widetilde{R}_l''(r) + \frac{l(l+1)}{2r^2}\widetilde{R}_l(r) + \widetilde{W}(r)\widetilde{R}_l(r) = \epsilon_l \widetilde{R}_l(r), \tag{3.48}$$

$$\int_{\mathbb{R}} \widetilde{R}_l^2 = 1, \tag{3.49}$$

$$\widetilde{R}_l = R_l \quad \textit{on } (r_{\mathrm{c}}, +\infty), \tag{3.50}$$

$$\widetilde{R}_l \geq 0 \quad \textit{on } (0, +\infty), \tag{3.51}$$

$$\sigma\left(\left(-\frac{1}{2}\Delta + \widetilde{W}\right)\Big|_{\mathcal{H}_l}\right) \setminus \{\epsilon_l\} \subset [E_+, +\infty). \tag{3.52}$$

Proof. Using the notation and the results in Lemma 38, we see that ϵ_l is an eigenvalue of $(T_{W,0})|_{\mathcal{H}_l}$, so that $E_+ \in (\min(\sigma(T_{W,0})), 0)$, which implies that there exists a unique positive real number r_{c}^+ such that $\mathcal{T}_W(r_{\mathrm{c}}^+) = E_+$. Let $r_{\mathrm{c}} > r_{\mathrm{c}}^+$ and $m_{\mathrm{c}} = \int_0^{r_{\mathrm{c}}} R_l^2$. We denote by R the unique odd function in $H^1(-r_c, r_c)$ such that

$$-\frac{1}{2}R'' + \frac{l(l+1)}{2r^2}R - \epsilon_l R = 0, \quad R(r_{\mathrm{c}}) = 1,$$

and by

$$F(d) = \int_0^{r_c - d} R^2(r)dr.$$

Note that the function $u(\mathbf{r}) = \frac{r_{\mathrm{c}} R(|\mathbf{r}|)}{|\mathbf{r}|}\mathcal{Y}_l^m(\frac{\mathbf{r}}{|\mathbf{r}|})$ is the unique solution in $H^1(B_{r_{\mathrm{c}}})$ to the boundary value problem $-\frac{1}{2}\Delta u - \epsilon_l u = 0$ in $B_{r_{\mathrm{c}}}$, $u|_{\partial B_{r_{\mathrm{c}}}} = \mathcal{Y}_l^m$, and that $F(d) = r_{\mathrm{c}}^{-2}\int_{B_{r_{\mathrm{c}}-d}} |u|^2$. For all $0 < \alpha \ll 1 \ll A < \infty$, we introduce

$$\theta^-_{\alpha,A} = \arcsin(\alpha/A), \quad \theta^+_{\alpha,A} = \pi - \arcsin(R_l(r_{\mathrm{c}})/A) - \theta^-_{\alpha,A},$$

$d_{\alpha,A}$ the unique solution in $(0, r_{\mathrm{c}})$ of

$$\alpha^2 F(d) + A^2 \frac{d}{2}\left(1 - \frac{\sin(2(\theta^+_{\alpha,A} + \theta^-_{\alpha,A})) - \sin(2\theta^-_{\alpha,A})}{2\theta^+_{\alpha,A}}\right) = m_{\mathrm{c}},$$

$$k_{\alpha,A} = \frac{\theta^+_{\alpha,A}}{d_{\alpha,A}}, \quad v_{\alpha,A} = \epsilon_l - \frac{k^2_{\alpha,A}}{2},$$

$$\beta^-_{\alpha,A} = \frac{k_{\alpha,A} A\cos(\theta^-_{\alpha,A})}{2\alpha} - \frac{R'(r_c - d_{\alpha,A})}{2R(r_c - d_{\alpha,A})}, \quad \beta^+_{\alpha,A} = \frac{R_l'(r_c) - k_{\alpha,A}A\cos(\theta^+_{\alpha,A} + \theta^-_{\alpha,A})}{2R_l(r_c)}.$$

When $\alpha \to 0^+$ and $A \to +\infty$, the above quantities behave as follows

$$\theta^-_{\alpha,A} \to 0^+, \quad \theta^+_{\alpha,A} \to \pi^-, \quad d_{\alpha,A} \sim \frac{2m_{\mathrm{c}}}{A^2}, \quad k_{\alpha,A} \sim \frac{\pi A^2}{2m_{\mathrm{c}}}, \quad v_{\alpha,A} \sim -\frac{\pi^2 A^4}{8m_{\mathrm{c}}^2},$$
$$\beta^-_{\alpha,A} \sim \frac{\pi A^3}{4m_{\mathrm{c}}\alpha}, \quad \beta^+_{\alpha,A} \sim \frac{\pi A^3}{4m_{\mathrm{c}}R_l(r_{\mathrm{c}})}. \tag{3.53}$$

Consider the function $R_{\alpha,A} \in H^1_{\rm o}(\mathbb{R})$ defined on $(0,+\infty)$ by

$$R_{\alpha,A} = \alpha \frac{R}{R(r_{\rm c}-d_{\alpha,A})} \mathbb{1}_{(0,r_{\rm c}-d_{\alpha,A})} + A \sin\left(k_{\alpha,A}(r-r_{\rm c}) + \theta^-_{\alpha,A} + \theta^+_{\alpha,A}\right) \mathbb{1}_{(r_{\rm c}-d_{\alpha,A},r_{\rm c})} + R_l \mathbb{1}_{(r_{\rm c},+\infty)}.$$

It is easily checked that $\widetilde{R}_l = R_{\alpha,A}$ is solution of (3.47)-(3.51) for $\widetilde{W} = W_{\alpha,A} \in H^{-1}_{\rm r}(\mathbb{R}^3)$, with radial representation given by

$$W_{\alpha,A} = \beta^-_{\alpha,A}\delta_{r_{\rm c}-d_{\alpha,A}} + \left(v_{\alpha,A} - \frac{l(l+1)}{2r^2}\right)\mathbb{1}_{(r_{\rm c}-d_{\alpha,A},r_{\rm c})} + \beta^+_{\alpha,A}\delta_{r_{\rm c}} + W\mathbb{1}_{(r_{\rm c},+\infty)}.$$

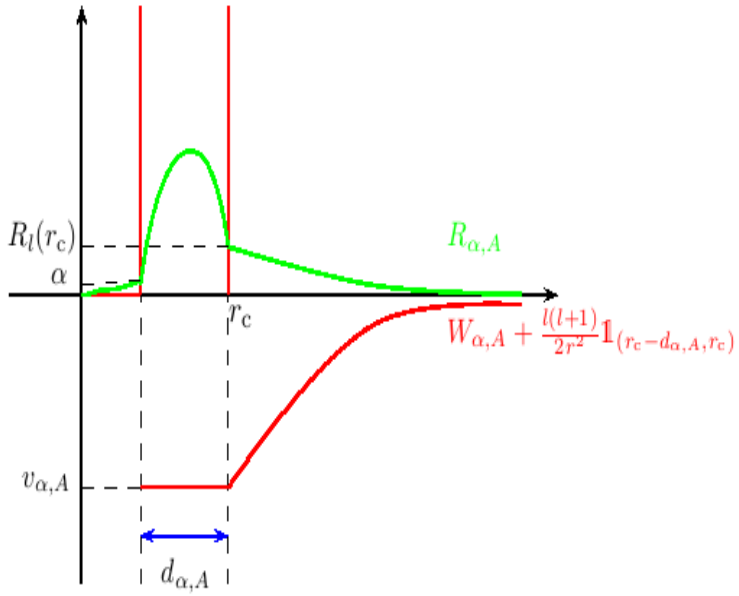


Figure 3.2 – Sketch of the function $R_{\alpha,A}$ (green) and of the potential $W_{\alpha,A} + \frac{l(l+1)}{2r^2}\mathbb{1}_{(r_{\rm c}-d_{\alpha,A},r_{\rm c})}$ (red).

Denoting by

$$H_{\alpha,A} = -\frac{1}{2}\Delta + W_{\alpha,A},$$

we are going to show that for $\alpha > 0$ small enough and $A < +\infty$ large enough

$$\sigma\left(H_{\alpha,A}\Big|_{\mathcal{H}_l}\right) \setminus \{\epsilon_l\} \subset (E_+, +\infty).$$

Let $\mu_{\alpha,A} = \min\left(\sigma\left(H_{\alpha,A}\Big|_{\mathcal{H}_l}\right) \setminus \{\epsilon_l\}\right)$. Assume that $\mu_{\alpha,A} \leq E_+$. As $\sigma_{\rm ess}(H_{\alpha,A}|_{\mathcal{H}_l}) = \mathbb{R}_+$, $\mu_{\alpha,A}$ is a discrete eigenvalue of $H_{\alpha,A}|_{\mathcal{H}_l}$. We denote by $U_{\alpha,A}$ an associated normalized eigenfunction and by $u_{\alpha,A} \in H^1_{\rm o}(\mathbb{R})$ the odd extension of its radial component multiplied by r. As $\mu_{\alpha,A}$ is in fact the second lowest eigenvalue of $H_{\alpha,A}|_{\mathcal{H}_l}$ (counting multiplicities), the function $u_{\alpha,A}$ satisfies

$$-\frac{1}{2}u''_{\alpha,A} + \frac{l(l+1)}{2r^2}u_{\alpha,A} + W_{\alpha,A}u_{\alpha,A} = \mu_{\alpha,A}u_{\alpha,A},$$

and has exactly one node $r^0_{\alpha,A}$ in $(0,+\infty)$. This node cannot lay in the interval $[r_{\rm c},+\infty)$; otherwise, the function $\phi(\mathbf{r}) = U_{\alpha,A}(\mathbf{r})\mathbb{1}_{[r^0_{\alpha,A},+\infty)}(|\mathbf{r}|)\mathcal{Y}^0_l\left(\frac{\mathbf{r}}{|\mathbf{r}|}\right)$ would belong to $H^1_0(\Omega(r^0_{\alpha,A}))\backslash\{0\}$ and we would have

$$E_+ = \mathcal{T}_W(r_{\rm c}^+) < \mathcal{T}_W(r^0_{\alpha,A}) \leq \frac{\langle\phi|T_{W,r^0_{\alpha,A}}|\phi\rangle}{\langle\phi|\phi\rangle} = \mu_{\alpha,A},$$

which contradicts the assumption that $\mu_{\alpha,A} \leq E_+$. It cannot either lay in the interval $(0, r_{\rm c} - d_{\alpha,A}]$; otherwise, as the potential $W_{\alpha,A}$ is equal to zero on this interval, we would have

$$\frac{1}{2}\int_0^{r^0_{\alpha,A}} |u'_{\alpha,A}|^2 + \frac{l(l+1)}{2}\int_0^{r^0_{\alpha,A}} \frac{|u_{\alpha,A}(r)|^2}{r^2}\,dr = \mu_{\alpha,A}\int_0^{r^0_{\alpha,A}} |u_{\alpha,A}|^2 < 0,$$

which is obviously not possible. We therefore have $r_{\alpha,A} \in (r_{\rm c} - d_{\alpha,A}, r_{\rm c})$, and without loss of generality, we can assume that $u_{\alpha,A}$ is positive in the neighborhood of $+\infty$. As $W_{\alpha,A}$ is equal to zero on $(0, r_{\rm c} - d_{\alpha,A})$, $u_{\alpha,A}$ is negative and concave on this interval, so that $u_{\alpha,A}(r_{\rm c} - d_{\alpha,A}) < 0$ and $u'_{\alpha,A}((r_{\rm c} - d_{\alpha,A})^+) < u'_{\alpha,A}((r_{\rm c} - d_{\alpha,A})^-) < 0$. We therefore have

$$\forall r \in [r_{\rm c} - d_{\alpha,A}, r_{\rm c}], \quad u_{\alpha,A} = \widetilde{A}_{\alpha,A}\sin\left(\widetilde{k}_{\alpha,A}(r - (r_{\rm c} - d_{\alpha,A})) + \widetilde{\theta}_{\alpha,A}\right),$$

with $\widetilde{A}_{\alpha,A} < 0$, $\widetilde{k}_{\alpha,A} = \sqrt{2(\mu_{\alpha,A} - v_{\alpha,A})}$, $0 < \widetilde{\theta}_{\alpha,A} < \pi/2$ and $\pi < \widetilde{k}_{\alpha,A}d_{\alpha,A} + \widetilde{\theta}_{\alpha,A} < 2\pi$. It follows from the jump condition at $r_{\rm c} - d_{\alpha,A}$ and from the fact that $u_{\alpha,A}$ is negative and concave on $(0, r_{\rm c} - d_{\alpha,A})$ that

$$\frac{\widetilde{k}_{\alpha,A}}{\tan(\widetilde{\theta}_{\alpha,A})} = \frac{u'_{\alpha,A}((r_{\rm c} - d_{\alpha,A})^+)}{u_{\alpha,A}(r_{\rm c} - d_{\alpha,A})} \geq \frac{u'_{\alpha,A}((r_{\rm c} - d_{\alpha,A})^+) - u'_{\alpha,A}((r_{\rm c} - d_{\alpha,A})^-)}{u_{\alpha,A}(r_{\rm c} - d_{\alpha,A})} = \beta^-_{\alpha,A}.$$

Thus,

$$\tan(\widetilde{\theta}_{\alpha,A}) \leq \frac{\widetilde{k}_{\alpha,A}}{\beta^-_{\alpha,A}} \leq \frac{2\pi}{\beta^-_{\alpha,A}d_{\alpha,A}} \sim \frac{4\alpha}{A}, \quad \text{when } \alpha \to 0^+ \text{ and } A \to +\infty. \tag{3.54}$$

We can distinguish two cases:

- case 1: $u'_{\alpha,A}(r_c - 0) < 0$. In this case, $\widetilde{k}_{\alpha,A}d_{\alpha,A} + \widetilde{\theta}_{\alpha,A} > \frac{3\pi}{2}$, which, together with (3.54), implies that for $\alpha > 0$ small enough and $A > 0$ large enough,

$$\widetilde{k}_{\alpha,A} \geq \frac{5}{4}k_{\alpha,A} \quad \text{or equivalently} \quad \mu_{\alpha,A} \geq \epsilon_l - \frac{9}{16}v_{\alpha,A} \sim \frac{9\pi^2A^4}{128m_{\rm c}^2},$$

  which contradicts the assumption that $\mu_{\alpha,A} \leq E_+$;

- case 2: $u'_{\alpha,A}(r_c - 0) \geq 0$. In this case, the function $u_{\alpha,A}$ is positive on $(r_{\rm c},+\infty)$ and the pair $(u_{\alpha,A}, \mu_{\alpha,A})$ is solution to the spectral problem on $(r_{\rm c},+\infty)$ with Robin boundary conditions

$$\begin{cases} -\frac{1}{2}u''_{\alpha,A}(r) + \frac{l(l+1)}{2r^2}u_{\alpha,A}(r) + Wu_{\alpha,A}(r) = \mu_{\alpha,A}u_{\alpha,A}(r), \quad r \in (r_{\rm c},+\infty) \\ u'_{\alpha,A}(r_c + 0) = \left(\frac{\widetilde{k}_{\alpha,A}}{\tan(\widetilde{k}_{\alpha,A}d_{\alpha,A} + \widetilde{\theta}_{\alpha,A})} + \beta^+_{\alpha,A}\right)u_{\alpha,A}(r_c). \end{cases} \tag{3.55}$$

When $\alpha \to 0^+$ and $A \to +\infty$, the parameter $\frac{\widetilde{k}_{\alpha,A}}{\tan(\widetilde{k}_{\alpha,A} d_{\alpha,A} + \widetilde{\theta}_{\alpha,A})} + \beta^+_{\alpha,A}$ goes to $+\infty$, so that $\mu_{\alpha,A}$ converges to the ground state eigenvalue of $T_{W,r_c}|_{\mathcal{H}_l}$, which implies

$$\lim_{\alpha \downarrow 0,\, A \to +\infty} \mu_{\alpha,A} = \mathcal{T}_W(r_c) > \mathcal{T}_W(r_c^+) = E_+.$$

Choosing $\alpha > 0$ small enough and A large enough, we obtain a contradiction with the assumption that $\mu_{\alpha,A} \leq E_+$.

We therefore have obtained a function $\widetilde{R}_l = R_{\alpha,A} \in H^1_{\rm o}(\mathbb{R})$ and a potential $\widetilde{W} = W_{\alpha,A} \in H^{-1}_{\rm r}(\mathbb{R}^3)$ such that (3.47)-(3.52) are satisfied. As $R_{\alpha,A}$ is in $C^\infty(\mathbb{R} \setminus \{\pm(r_{\rm c} - d_{\alpha,A}), \pm r_{\rm c}\})$ and is positive on $(0, +\infty)$, we can construct a sequence $(\widetilde{R}_{l,n})_{n\in\mathbb{N}}$ of odd functions of $C^\infty(\mathbb{R}) \cap H^1_{\rm o}(\mathbb{R})$ positive on $(0, +\infty)$ and converging in $H^1_{\rm o}(\mathbb{R})$ to $R_{\alpha,A}$, such that $\widetilde{R}_{l,n} = R_{\alpha,A} = R_l$ on $(r_{\rm c}, +\infty)$, $\widetilde{R}_{l,n} = R_{\alpha,A}$ on $(0, r_{\rm c} - d_{\alpha,A})$ and $\int_{\mathbb{R}} |\widetilde{R}_{l,n}|^2 = 1$. Consider the sequence of radial potentials defined by

$$\forall n \in \mathbb{N},\ \forall r \in (0, +\infty), \quad \widetilde{W}_n(r) = \epsilon_l + \frac{1}{2}\frac{\widetilde{R}''_{l,n}(r)}{\widetilde{R}_{l,n}(r)} - \frac{l(l+1)}{2r^2}.$$

As $\widetilde{R}_{l,n}(r)$ is bounded away from zero on the interval $[(r_c - d_{\alpha,A})/2, r_c + 1]$ uniformly in n, each $\widetilde{W}_n$ is in $H^s_{\rm r}(\mathbb{R}^3)$ for all $s \geq 0$, and the sequence $(\widetilde{W}_n)_{n\in\mathbb{N}}$ converges to $W_{\alpha,A}$ in $H^{-1}_{\rm r}(\mathbb{R}^3)$. Consequently, the Rayleigh quotients $\mathbf{R}_n(\phi) = \dfrac{\langle\phi| -\frac{1}{2}\Delta + \widetilde{W}_n|\phi\rangle}{\|\phi\|^2}$ converge to $\mathbf{R}(\phi) = \dfrac{\langle\phi| -\frac{1}{2}\Delta + \widetilde{W}|\phi\rangle}{\|\phi\|^2}$ for any $\phi \in \mathcal{H}_l \cap H^1(\mathbb{R}^3)$, which implies, by the minmax principle, that the $k^{\rm th}$ negative eigenvalue of $\left(-\frac{1}{2}\Delta + \widetilde{W}_n\right)\Big|_{\mathcal{H}_l}$ converges to the $k^{\rm th}$ negative eigenvalue of $\left(-\frac{1}{2}\Delta + W_{\alpha,A}\right)\big|_{\mathcal{H}_l}$ when n goes to infinity. Therefore, for n large enough, conditions (3.47)-(3.52) are satisfied for $\widetilde{W} = \widetilde{W}_n$. □

We are now in position to prove the non-emptiness of $\mathcal{M}_{z,\Delta E,r_{\rm c},s}$ under the assumptions of Lemma 30. Applying Lemma 39 successively for each $0 \leq l \leq l_z$ with $W = W_z^{\rm AA}$, $R_l = R_{z,n^\star_{z,l},l}$, $\epsilon_l = \epsilon_{z,n^\star_{z,l},l}$ and $r_{\rm c} > r^+_{z,{\rm c}}$, we obtain $l_z + 1$ functions $\widetilde{W}_l \in H^s_{\rm r}(\mathbb{R}^3)$ and $l_z + 1$ functions $\widetilde{R}_l$, satisfying for each $0 \leq l \leq l_z$,

$$\widetilde{R}_l \in H^1_{\rm o}(\mathbb{R}), \tag{3.56}$$

$$-\frac{1}{2}\widetilde{R}''_l(r) + \frac{l(l+1)}{2r^2}\widetilde{R}_l(r) + \widetilde{W}_l\widetilde{R}_l(r) = \epsilon_{z,n^\star_{z,l},l}\widetilde{R}_l(r), \tag{3.57}$$

$$\int_{\mathbb{R}} \widetilde{R}_l^2 = 1, \tag{3.58}$$

$$\widetilde{R}_l = R_{z,n^\star_{z,l},l} \quad \text{and} \quad \widetilde{W}_l = W_z^{\rm AA} \quad \text{on } (r_{\rm c}, +\infty), \tag{3.59}$$

$$\widetilde{R}_l \geq 0 \quad \text{on } (0, +\infty). \tag{3.60}$$

We then introduce the functions

$$\widetilde{\phi}_l^m(\mathbf{r}) = \frac{\sqrt{2}\,\widetilde{R}_l(|\mathbf{r}|)}{|\mathbf{r}|}\mathcal{Y}_l^m\left(\frac{\mathbf{r}}{|\mathbf{r}|}\right), \qquad -l \leq m \leq l, \tag{3.61}$$

and the density

$$\widetilde{\rho}^0(\mathbf{r}) = \sum_{l=0}^{l_z} \sum_{m=-l}^{l} p_{z,n^\star_{z,l},l} |\widetilde{\phi}^m_l(\mathbf{r})|^2,$$

and we consider a sequence $(W_{\mathrm{loc},k})_{k\geq 1}$ of local potentials in the class $H^s_{\mathrm{r}}(\mathbb{R}^3)$ such that $W_{\mathrm{loc},k} \geq W^{\mathrm{AA}}_z$ on $\mathbb{R}^3$, $W_{\mathrm{loc},k} = W^{\mathrm{AA}}_z$ in $\Omega(r_{\mathrm{c}})$ and $W_{\mathrm{loc},k} = k$ on $B_{r_{\mathrm{c}}-1/k}$. We finally set

$$V_{\mathrm{loc},k} = W_{\mathrm{loc},k} - \widetilde{\rho}^0 \star |\cdot|^{-1} \quad \text{and} \quad \forall 0 \leq l \leq l_z, \quad V_{l,k} = \widetilde{W}_l - W_{\mathrm{loc},k},$$

and

$$V_k = V_{\mathrm{loc},k} + \sum_{l=0}^{l_z} P_l V_{l,k} P_l.$$

By construction, the self-adjoint operator

$$H_k = -\frac{1}{2}\Delta + V_k + \widetilde{\rho}^0 \star |\cdot|^{-1},$$

on $L^2(\mathbb{R}^3)$ is rotation-invariant, and for all $0 \leq l \leq l_z$,

$$\mathbb{1}_{(-\infty,E_+)}(H_k|_{\mathcal{H}_l}) = \mathbb{1}_{(-\infty,E_+)}\left(\left(-\frac{1}{2}\Delta + \widetilde{W}_l\right)\Big|_{\mathcal{H}_l}\right) = \sum_{m=-l}^{l} |\widetilde{\phi}^m_l\rangle\langle\widetilde{\phi}^m_l|.$$

Lastly, for all $l > l_z$,

$$\min\sigma(H_k|_{\mathcal{H}_l}) \geq \min\sigma\left(-\frac{1}{2}\Delta + W_{\mathrm{loc},k}\right) \underset{k\to\infty}{\longrightarrow} \mathcal{T}_{W^{\mathrm{AA}}_z}(r_{\mathrm{c}}) > \mathcal{T}_{W^{\mathrm{AA}}_z}(r^+_{z,\mathrm{c}}) = E_+.$$

Therefore, for k large enough, $V_k \in \mathcal{M}_{z,\Delta E,r_{\mathrm{c}},s}$.

3.5.4 Proof of Theorem 31

Let us prove that $\mathcal{M}_{z,\Delta E,r_{\mathrm{c}},s}$ is weakly closed in the affine space $\mathcal{X}_{z,\Delta E,r_{\mathrm{c}},s}$. For this purpose, we consider a sequence $(V^{\mathrm{PP}}_{z,k})_{k\in\mathbb{N}}$ of elements of $\mathcal{M}_{z,\Delta E,r_{\mathrm{c}},s}$ weakly converging to some V^{PP}_z in $\mathcal{X}_{z,\Delta E,r_{\mathrm{c}},s}$. We denote by $H^{\mathrm{PP}}_{z,k}$ the Hartree pseudo-Hamiltonian obtained with the pseudopotential $V^{\mathrm{PP}}_{z,k}$ and by $\widetilde{\phi}^m_{z,l,k}$ its eigenfunctions of the form (3.26). We have for all $k \in \mathbb{N}$,

$$H^{\mathrm{PP}}_{z,k} = -\frac{1}{2}\Delta + W_k, \qquad H^{\mathrm{PP}}_{z,k}\widetilde{\phi}^m_{z,l,k} = \epsilon_{z,n^\star_{z,l},l}\widetilde{\phi}^m_{z,l,k}, \qquad \|\widetilde{\phi}^m_{z,l,k}\|_{L^2} = 1, \tag{3.62}$$

$$\widetilde{\rho}_k(\mathbf{r}) = \sum_{l=0}^{l_z}\sum_{m=-l}^{l} p_{z,n^\star_{z,l},l}|\widetilde{\phi}^m_{z,l,k}(\mathbf{r})|^2, \qquad v_k = \widetilde{\rho}_k \star |\cdot|^{-1},$$

$$W_k = V_{z,\mathrm{loc},k} + v_k + \sum_{l=0}^{l_z} P_l V_{z,l,k} P_l.$$

Note that for all $0 \leq l \leq l_z$, $-l \leq m \leq l$, and $k \in \mathbb{N}$, we have $\widetilde{\phi}^m_{z,l,k} = \phi^m_{z,n^\star_{z,l},l}$ on $\mathbb{R}^3 \setminus B_{r_{\mathrm{c}}}$ and

$$(W_k\widetilde{\phi}^m_{z,l,k})(\mathbf{r}) = \begin{cases} W^{\mathrm{AA}}_z(\mathbf{r})\phi^m_{z,n^\star_{z,l},l}(\mathbf{r}) & \text{if } |\mathbf{r}| \geq r_{\mathrm{c}}, \\ (V_{z,\mathrm{loc},k}(\mathbf{r}) + v_k(\mathbf{r}) + V_{z,l,k}(\mathbf{r}))\widetilde{\phi}^m_{z,l,k}(\mathbf{r}) & \text{if } |\mathbf{r}| < r_{\mathrm{c}}. \end{cases}$$

As $\epsilon_{z,n^\star_{z,l},l} < 0$, $v_k \geq 0$ in $\mathbb{R}^3$, and $\|\widetilde{\phi}^m_{z,l,k}\|_{L^2} = 1$ we obtain, using the Sobolev inequality in $\mathbb{R}^3$, the boundedness of the sequence $(\|V_{z,l,k}\|_{L^2})_{k\in\mathbb{N}}$ and Lemma 37, that for all $k \in \mathbb{N}$,

$$\begin{aligned}
\frac{1}{2}\|\nabla\widetilde{\phi}^m_{z,l,k}\|^2_{L^2} &= -\langle\widetilde{\phi}^m_{z,l,k}|W_k|\widetilde{\phi}^m_{z,l,k}\rangle + \epsilon_{z,n^\star_{z,l},l} \\
&\leq -\int_{B_{r_\mathrm{c}}}(V_{z,\mathrm{loc},k}+V_{z,l,k})|\widetilde{\phi}^m_{z,l,k}|^2 - \int_{\mathbb{R}^3\setminus B_{r_\mathrm{c}}} W^{\mathrm{AA}}_z|\phi^m_{z,n^\star_{z,l},l}|^2 \\
&\leq \left(\|V_{z,\mathrm{loc},k}+V_{z,l,k}\|_{L^2}\|\widetilde{\phi}^m_{z,l,k}\|^{1/2}_{L^2}\|\widetilde{\phi}^m_{z,l,k}\|^{3/2}_{L^6} + \|W^{\mathrm{AA}}_z\|_{L^\infty(\mathbb{R}^3\setminus B_{r_\mathrm{c}})}\right) \\
&\leq C(1+\|\nabla\widetilde{\phi}^m_{z,l,k}\|^{3/2}_{L^2}),
\end{aligned}$$

where the constant C is independent of k. This implies that for all $0 \leq l \leq l_z$ and all $-l \leq m \leq l$, the sequence $(\widetilde{\phi}^m_{z,l,k})_{k\in\mathbb{N}}$ is bounded in $H^1(\mathbb{R}^3)$. We can therefore extract from $(\widetilde{\phi}^m_{z,l,k})_{k\in\mathbb{N}}$ a subsequence $(\widetilde{\phi}^m_{z,l,k_n})_{n\in\mathbb{N}}$ which weakly converges in $H^1(\mathbb{R}^3)$ to some function $\widetilde{\phi}^m_{z,l} \in H^1(\mathbb{R}^3)\cap\mathcal{H}_l$. As for all $k \in \mathbb{N}$, $\widetilde{\phi}^m_{z,l,k} = \phi^m_{z,n^\star_{z,l},l}$ in $\mathbb{R}^3\setminus B_{r_\mathrm{c}}$, we can assume, without loss of generality, that the convergence of $(\widetilde{\phi}^m_{z,l,k_n})_{n\in\mathbb{N}}$ to $\widetilde{\phi}^m_{z,l}$ also holds strongly in $L^p(\mathbb{R}^3)$ for all $1 \leq p < 6$ and almost everywhere in $\mathbb{R}^3$. In particular,

$$\forall 0 \leq l,l' \leq l_z, \quad \forall -l \leq m \leq l, \quad \forall -l' \leq m' \leq l', \quad \int_{\mathbb{R}^3}\widetilde{\phi}^m_{z,l}\widetilde{\phi}^{m'}_{z,l'} = \delta_{ll'}\delta_{mm'},$$

and the associated functions $\widetilde{R}_{z,l}$ defined by (3.26) satisfy (3.27) and (3.29)-(3.31). We also infer from the strong convergence of $(\widetilde{\phi}^m_{z,l,k_n})_{n\in\mathbb{N}}$ to $\widetilde{\phi}^m_{z,l}$ in $L^2(\mathbb{R}^3)\cap L^4(\mathbb{R}^3)$ that the sequence $(\widetilde{\rho}_{k_n})_{n\in\mathbb{N}}$ strongly converges in $L^1(\mathbb{R}^3)\cap L^2(\mathbb{R}^3)$, hence in $L^{6/5}(\mathbb{R}^3)$ to the function $\widetilde{\rho}$ defined by

$$\widetilde{\rho}(\mathbf{r}) = \sum_{l=0}^{l_z}\sum_{m=-l}^{l} p_{z,n^\star_{z,l},l}|\widetilde{\phi}^m_{z,l}(\mathbf{r})|^2,$$

which, in turn, implies that the sequence $(v_{k_n})_{n\in\mathbb{N}}$ strongly converges in $\mathcal{C}'$, hence in $L^6(\mathbb{R}^3)$, to the function $v = \widetilde{\rho}\star|\cdot|^{-1}$. Lastly, as $(V_{z,l,k_n})_{n\in\mathbb{N}}$ weakly converges to $V_{z,l}$ in $H^s_{0,r}(B_{r_\mathrm{c}})$ for $s > 0$, we can assume without loss of generality that the sequence $(V_{z,l,k_n})_{k_n\in\mathbb{N}}$ strongly converges to $V_{z,l}$ in $L^2(B_{r_\mathrm{c}})$. Passing to the limit in (3.62), we obtain that the functions $\widetilde{R}_{z,l}$ satisfy

$$-\frac{1}{2}\widetilde{R}''_{z,l}(r) + \frac{l(l+1)}{2r^2}\widetilde{R}_{z,l}(r) + (v(r)+V_{z,l}(r))\,\widetilde{R}_{z,l}(r) = \epsilon_{z,n^\star_{z,l},l}\widetilde{R}_{z,l}(r).$$

To conclude that $V^{\mathrm{PP}}_z \in \mathcal{M}_{z,\Delta E,r_\mathrm{c},s}$, we just need to show that

$$\mathbb{1}_{(-\infty,E_+)}(H^{\mathrm{PP}}_z) = \sum_{l=0}^{l_z}\sum_{m=-l}^{l}|\widetilde{\phi}^m_{z,l}\rangle\langle\widetilde{\phi}^m_{z,l}|, \tag{3.63}$$

where $H^{\mathrm{PP}}_z = -\frac{1}{2}\Delta + V^{\mathrm{PP}}_z + v$. If this was not the case, there would exists $\lambda < E_+$ and

$$\phi \in H^2(\mathbb{R}^3)\cap\left(\mathrm{Span}\left\{\widetilde{\phi}^m_{z,l},\ 0\leq l\leq l_z,\ -l\leq m\leq l\right\}\right)^\perp$$

such that $\|\phi\|_{L^2} = 1$ and $H_z^{\mathrm{PP}}\phi = \lambda\phi$. Consider, for n large enough, the function

$$\phi_n = \frac{\phi - \sum_{l=0}^{l_z}\sum_{m=-l}^{l}(\widetilde{\phi}^m_{z,l,k_n},\phi)_{L^2}\widetilde{\phi}^m_{z,l,k_n}}{\left\|\phi - \sum_{l=0}^{l_z}\sum_{m=-l}^{l}(\widetilde{\phi}^m_{z,l,k_n},\phi)_{L^2}\widetilde{\phi}^m_{z,l,k_n}\right\|_{L^2}}.$$

We have

$$\phi_n \in H^2(\mathbb{R}^3) \cap \left(\mathrm{Span}\left\{\widetilde{\phi}^m_{z,l,k_n},\ 0 \le l \le l_z,\ -l \le m \le l\right\}\right)^{\perp}, \qquad \|\phi_n\|_{L^2} = 1, \tag{3.64}$$

and

$$\langle\phi_n|H^{\mathrm{PP}}_{z,k_n}|\phi_n\rangle = \frac{\lambda + \langle\phi|(V_{z,\mathrm{loc},k_n}+V_{z,l,k_n})-(V_{z,\mathrm{loc}}+V_{z,l})|\phi\rangle + \int_{\mathbb{R}^3}(v_{k_n}-v)\phi^2 - \sum_{l=0}^{l_z}\sum_{m=-l}^{l}\epsilon_{z,n^\star_{z,l},l}|(\widetilde{\phi}^m_{z,l,k_n},\phi)_{L^2}|^2}{\left\|\phi - \sum_{l=0}^{l_z}\sum_{m=-l}^{l}(\widetilde{\phi}^m_{z,l,k_n},\phi)_{L^2}\widetilde{\phi}^m_{z,l,k_n}\right\|^2_{L^2}}.$$

Using the weak convergence of V^{PP}_{z,k_n} to V^{PP}_z in $\mathcal{X}_{z,\Delta E,r_{\mathrm{c}},s}$, the strong convergence of v_{k_n} to v in $L^2(\mathbb{R}^3)$ and the strong convergence of $\widetilde{\phi}^m_{z,l,k_n}$ to $\widetilde{\phi}^m_{z,l}$ in $L^2(\mathbb{R}^3)$, we obtain that

$$\lim_{n\to\infty}\langle\phi_n|H^{\mathrm{PP}}_{z,k_n}|\phi_n\rangle = \lambda.$$

Together with (3.62) and (3.64), this implies that for n large enough, H^{PP}_{z,k_n} has at least $(l_z+1)^2+1$ eigenvalues in $(-\infty, E_+)$, which contradicts the fact that $V^{\mathrm{PP}}_{z,k_n} \in \mathcal{M}_{z,\Delta E,r_{\mathrm{c}},s}$. Therefore, $V^{\mathrm{PP}}_z \in \mathcal{M}_{z,\Delta E,r_{\mathrm{c}},s}$, which proves that $\mathcal{M}_{z,\Delta E,r_{\mathrm{c}},s}$ is weakly closed in $\mathcal{X}_{z,\Delta E,r_{\mathrm{c}},s}$.

3.5.5 Proof of Lemma 32

The function $\widetilde{\phi}_{z,l,m}$ is an eigenfunction of the Schrödinger operator $-\frac{1}{2}\Delta + W_{z,\mathrm{loc}} + V_{z,l}$ on $L^2(\mathbb{R}^3)$, with $W_{z,\mathrm{loc}}+V_{z,l} \in H^s_{\mathrm{r}}(\mathbb{R}^3)$. By elliptic regularity, $\widetilde{\phi}_{z,n,l} \in H^{s+2}(\mathbb{R}^3)$, and therefore $\widetilde{R}_{z,l} \in H^{s+2}_{\mathrm{o}}(\mathbb{R})$ in view of Lemma 26. It follows from the unique continuation principle for nonnegative solutions of second-order ordinary differential equations that $\widetilde{R}_{z,l} > 0$ on $(0,+\infty)$. The function $\widetilde{R}_{z,l}$ is an odd function which solves a differential equation, with regular singular point, of the form

$$r^2y'' - l(l+1)y + V_l(r)y = 0, \quad \text{with} \quad V_l(0) = 0. \tag{3.65}$$

Its indicial equation is

$$s(s-1) - l(l+1) = 0,$$

with roots $s_1 = l+1$ and $s_2 = -l$. Since $s_1 - s_2 = 2l+1$ is an integer, Fuch's theorem [46, 93] states that the fundamental system of solutions of (3.65) is

$$\begin{cases} y_1(r) = r^{s_1}p(r) \\ y_2(r) = c\,p(r)r^{s_1}\ln(r) + r^{s_2}q(r), \end{cases}$$

where $p(0) \neq 0$, $q(0) \neq 0$ and c is a constant. As y_2 does not vanish at zero, $\widetilde{R}_{z,l}$ is proportional to y_1.

3.5.6 Proof of Proposition 33

Observing that

$$E_{V_z^{\mathrm{PP}}}(\widetilde{\gamma}, v, W) = \mathrm{Tr}\,\left(\left(-\frac{1}{2}\Delta + V_z^{\mathrm{PP}}\right)\widetilde{\gamma}\right) + \frac{1}{2}D(\rho_{\widetilde{\gamma}}, \rho_{\widetilde{\gamma}}) + \mathrm{Tr}\,\left(\widetilde{\gamma}(v+W)\right)$$

allows us to follow the same lines as in the proofs of [23, Theorems 5 and 12] (see also the first point in [23, Section 5]). Indeed, the operator H_z^{PP} has the same spectral properties as the operator H_0 in [23], and the key property on the perturbation that we need to proceed as in [23] is that there exists a constant $C \in \mathbb{R}_+$ such that

$$|\mathrm{Tr}\,\left(\widetilde{\gamma}(v+W)\right)| \leq C\left(\|v\|_{X_{z,\Delta E,r_{\mathrm{c}},s}} + \|W\|_{\mathcal{C}'}\right)\|\widetilde{\gamma}\|_{\mathfrak{S}_{1,1}}, \tag{3.66}$$

for all $(\widetilde{\gamma}, v, W) \in \mathfrak{S}_{1,1} \times X_{z,\Delta E,r_{\mathrm{c}},s} \times \mathcal{C}'$. Let us prove that (3.66) actually holds true. On the one hand, we have for all $(\widetilde{\gamma}, W) \in \mathfrak{S}_{1,1} \times \mathcal{C}'$,

$$\begin{aligned}
|\mathrm{Tr}\,\left(\widetilde{\gamma}W\right)| &= \left|\mathrm{Tr}\,\left((1-\Delta)^{-1/2}(1-\Delta)^{1/2}\widetilde{\gamma}(1-\Delta)^{1/2}(1-\Delta)^{-1/2}W\right)\right| \\
&\leq \|(1-\Delta)^{-1/2}\|\,\|(1-\Delta)^{1/2}\widetilde{\gamma}(1-\Delta)^{1/2}\|_{\mathfrak{S}_1}\|(1-\Delta)^{-1/2}W\| \\
&\leq \|(1-\Delta)^{-1/2}\|\,\|(1-\Delta)^{1/2}\widetilde{\gamma}(1-\Delta)^{1/2}\|_{\mathfrak{S}_1}\|(1-\Delta)^{-1/2}W\|_{\mathfrak{S}_6} \\
&\leq C\|\widetilde{\gamma}\|_{\mathfrak{S}_{1,1}}\,\|W\|_{L^6} \leq C\|\widetilde{\gamma}\|_{\mathfrak{S}_{1,1}}\,\|W\|_{\mathcal{C}'},
\end{aligned}$$

where we have used the Kato-Seiler-Simon inequality [77] for $p = 6$. Likewise, we have for all $(\widetilde{\gamma}, v) \in \mathfrak{S}_{1,1} \times X_{z,\Delta E,r_{\mathrm{c}},s}$,

$$\begin{aligned}
|\mathrm{Tr}\,\left(\widetilde{\gamma}v\right)| &= \left|\mathrm{Tr}\,\left(\left(v_{\mathrm{loc}} + \sum_{l=0}^{l_z} P_l v_l P_l\right)\widetilde{\gamma}\right)\right| \\
&\leq \left|\mathrm{Tr}\,\left((1-\Delta)^{-1/2}v_{\mathrm{loc}}(1-\Delta)^{-1/2}(1-\Delta)^{1/2}\widetilde{\gamma}(1-\Delta)^{1/2}\right)\right| \\
&\quad + \sum_{l=0}^{l_z}\left|\mathrm{Tr}\,\left(P_l(1-\Delta)^{-1/2}v_l(1-\Delta)^{-1/2}P_l(1-\Delta)^{1/2}\widetilde{\gamma}(1-\Delta)^{1/2}\right)\right| \\
&\leq C\|\widetilde{\gamma}\|_{\mathfrak{S}_{1,1}}\left(\|v_{\mathrm{loc}}\|_{L^2} + \sum_{l=0}^{l_z}\|v_l\|_{L^2}\right) \leq C\|\widetilde{\gamma}\|_{\mathfrak{S}_{1,1}}\,\|v\|_{X_{z,\Delta E,r_{\mathrm{c}},s}},
\end{aligned}$$

where we have used that the P_l's commute with the Laplace operator and the fact that for all $w \in L^2(\mathbb{R}^3)$,

$$\|(1-\Delta)^{-1/2}w(1-\Delta)^{-1/2}\| \leq \||w|^{1/2}(1-\Delta)^{-1/2}\|^2 \leq \||w|^{1/2}(1-\Delta)^{-1/2}\|_{\mathfrak{S}_4}^2 \leq C\|w\|_{L^2},$$

by the Kato-Seiler-Simon inequality for $p = 4$.

Proceeding as in the proofs of Theorems 5 (non-degenerate case) and 12 (degenerate case) in [23], we obtain that there exists $\eta > 0$ such that for all $(v, W) \in B_\eta(X_{z,\Delta E,r_{\mathrm{c}},s}) \times B_\eta(\mathcal{C}')$, problem (3.37) has a unique minimizer $\widetilde{\gamma}_{v+W}(V_z^{\mathrm{PP}})$ and that, for each $V_z^{\mathrm{PP}} \in \mathcal{M}_{z,\Delta E,r_{\mathrm{c}},s}$, the function $(v+W) \mapsto \widetilde{\gamma}_{v+W}(V_z^{\mathrm{PP}})$ is real analytic from $B_\eta(X_{z,\Delta E,r_{\mathrm{c}},s}) + B_\eta(\mathcal{C}')$ to $\mathfrak{S}_{1,1}$. Expanding $\alpha \mapsto \widetilde{\gamma}_{\alpha(v+W)}(V_z^{\mathrm{PP}})$ as

$$\widetilde{\gamma}_{\alpha(v+W)}(V_z^{\mathrm{PP}}) = \widetilde{\gamma}_z^0 + \sum_{k=1}^{+\infty}\alpha^k\gamma_{v+W}^{(k)}(V_z^{\mathrm{PP}}),$$

the coefficients $\widetilde{\gamma}_{v,W}^{(j,k)}(V_z^{\rm PP})$ in (3.38) are connected to the coefficients $\gamma_{v+W}^{(k)}(V_z^{\rm PP})$ in the above expansion by the relation

$$\gamma_{\alpha v+\beta W}^{(k)}(V_z^{\rm PP}) = \sum_{j=0}^{k} \alpha^j \beta^{k-j} \widetilde{\gamma}_{v,W}^{(j,k-j)}(V_z^{\rm PP}).$$

3.5.7 Proof of Theorem 34

It suffices to prove the results in the degenerate case, since, in this setting, the non-degenerate case can be seen as a special case of the degenerate case (take $N_{\rm p} = 0$ in [23, Section 4]). We can also restrict ourselves to the pseudopotential case, as the all-electron case works the same.

Let $V_{\rm ref} \in \mathcal{M}_{z,\Delta E,r_{\rm c},s}$ be a reference pseudopotential fixed once and for all and $M \in \mathbb{R}_+$. We are going to establish a series of uniform bounds valid for all $V_z^{\rm PP} \in \mathcal{M}_{z,\Delta E,r_{\rm c},s}$ satisfying

$$\|V_z^{\rm PP} - V_{\rm ref}\|_{X_{z,\Delta E,r_{\rm c},s}} \leq M. \tag{3.67}$$

In the sequel, we will denote by C_M constants depending on $V_{\rm ref}$ and on M, but not on $V_z^{\rm PP}$. It follows from the arguments used in Section 3.5.4 that the pseudo-orbitals associated with $V_z^{\rm PP}$ satisfy

$$\max_{0\leq l\leq l_z} \max_{|m|\leq l} \|\widetilde{\phi}_{z,l}^m\|_{H^1} \leq C_M,$$

which implies that $\|\widetilde{\rho}_z^0\|_{L^1\cap L^3} \leq C_M$, and therefore that $\|\widetilde{\rho}_z^0 \star |\cdot|^{-1}\|_{L^\infty} \leq C_M$, from which we infer that

$$\max_{0\leq l\leq l_z} \|W_{z,\rm loc} + V_{z,l}\|_{L^{3/2}} \leq C_M, \tag{3.68}$$

and finally that

$$\max_{0\leq l\leq l_z} \max_{|m|\leq l} \|\widetilde{\phi}_{z,l}^m\|_{L^\infty} \leq 2 \max_{0\leq l\leq l_z} \max_{|m|\leq l} \|\widetilde{\phi}_{z,l}^m\|_{H^2} \leq C_M. \tag{3.69}$$

Using the fact that $W_z^{\rm PP} = W_z^{\rm AA}$ in $\Omega(r_{\rm c})$ and the maximum principle for second-order elliptic equations [36], we obtain that

$$\max_{0\leq l\leq l_z} \max_{|m|\leq l} \|\widetilde{\phi}_{z,l}^m e^{\sqrt{|\epsilon_{z,\rm F}^0|}|\cdot|/2}\|_{L^\infty} \leq C_M. \tag{3.70}$$

As in [23], we decompose $L^2(\mathbb{R}^3)$ as the orthogonal sum of the fully occupied, partially occupied, and unoccupied spaces

$$L^2(\mathbb{R}^3) := \mathcal{H}_{\rm f} \oplus \mathcal{H}_{\rm p} \oplus \mathcal{H}_{\rm u}, \tag{3.71}$$

where $\mathcal{H}_{\rm f} = {\rm Ran}(\mathbb{1}_{(-\infty,\epsilon_{z,\rm F}^0)}(H_z^{\rm PP}))$, $\mathcal{H}_{\rm p} = {\rm Ran}(\mathbb{1}_{\{\epsilon_{z,\rm F}^0\}}(H_z^{\rm PP}))$ and $\mathcal{H}_{\rm u} = {\rm Ran}(\mathbb{1}_{(\epsilon_{z,\rm F}^0,+\infty)}(H_z^{\rm PP}))$, and where $P_{\rm f}$, $P_{\rm p}$ and $P_{\rm u}$ are the orthogonal projectors from $L^2(\mathbb{R}^3)$ to $\mathcal{H}_{\rm f}$, $\mathcal{H}_{\rm p}$ and $\mathcal{H}_{\rm u}$ respectively. We then introduce

- the spaces

$$\mathcal{A}_{\rm ux} := \left\{ A_{\rm ux} \in \mathcal{B}(\mathcal{H}_{\rm x}, \mathcal{H}_{\rm u}) \mid (P_{\rm u}(H_z^{\rm PP} - \epsilon_{\rm F}^0)P_{\rm u})^{1/2} A_{\rm ux} \in \mathcal{B}(\mathcal{H}_{\rm x}, \mathcal{H}_{\rm u}) \right\},$$

for $\mathrm{x} \in \{\mathrm{f}, \mathrm{p}\}$, endowed with the inner product

$$(A_{\mathrm{ux}}, B_{\mathrm{ux}})_{\mathcal{A}_{\mathrm{ux}}} := \mathrm{Tr}\,(A_{\mathrm{ux}}^* P_{\mathrm{u}} (H_z^{\mathrm{PP}} - \epsilon_{\mathrm{F}}^0) P_{\mathrm{u}} B_{\mathrm{ux}});$$

- the finite dimensional spaces

$$\mathcal{A}_{\mathrm{pf}} := \mathcal{B}(\mathcal{H}_{\mathrm{f}}, \mathcal{H}_{\mathrm{p}}) \quad \text{and} \quad \mathcal{A}_{\mathrm{pp}} := \{A_{\mathrm{pp}} \in \mathcal{S}(\mathcal{H}_{\mathrm{p}}) \mid \mathrm{Tr}\,(A_{\mathrm{pp}}) = 0\};$$

- the product space

$$\mathcal{A} := \mathcal{A}_{\mathrm{uf}} \times \mathcal{A}_{\mathrm{up}} \times \mathcal{A}_{\mathrm{pf}} \times \mathcal{A}_{\mathrm{pp}},$$

which we endow with the inner product

$$(A, B)_{\mathcal{A}} = \sum_{\mathrm{x} \in \{\mathrm{f},\mathrm{p}\}} (A_{\mathrm{ux}}, B_{\mathrm{ux}})_{\mathcal{A}_{\mathrm{ux}}} + \sum_{\mathrm{x} \in \{\mathrm{f},\mathrm{p}\}} \mathrm{Tr}\,\left(A_{\mathrm{px}} B_{\mathrm{px}}^*\right).$$

Note that the decomposition (3.71), as well as the space $\mathcal{A}$, depend on V_z^{PP}. Following [23, Eq. (43)], let us first show that the continuous linear map

$$\begin{aligned} \zeta : \mathcal{C}' &\to \mathcal{A}' \\ W &\mapsto -(P_{\mathrm{u}} W P_{\mathrm{f}}, P_{\mathrm{u}} W P_{\mathrm{p}} \Lambda, (2-\Lambda) P_{\mathrm{p}} W P_{\mathrm{f}}, P_{\mathrm{p}} W P_{\mathrm{p}}), \end{aligned}$$

where Λ is the diagonal matrix containing the partial occupation numbers at the Fermi level, can be extended in a unique way to a continuous linear map from $\mathcal{C}' + L^2_{\mathrm{w}}$ to $\mathcal{A}'$. We first observe that for all $W \in C^\infty_{\mathrm{c}}(\mathbb{R}^3)$ (where $C^\infty_{\mathrm{c}}(\mathbb{R}^3)$ is the space of the C^∞ functions on $\mathbb{R}^3$ with compact support), and all $A \in \mathcal{A}$,

$$\begin{aligned} |\mathrm{Tr}\,((P_{\mathrm{u}} W P_{\mathrm{f}})^* A_{uf})| &= |\mathrm{Tr}\,(P_{\mathrm{f}} W P_{\mathrm{u}} A_{\mathrm{uf}})| \\ &= \left|\mathrm{Tr}\,\left(P_{\mathrm{f}} W (H_z^{\mathrm{PP}} - \epsilon_{\mathrm{F}}^0)\big|_{\mathcal{H}_{\mathrm{u}}}^{-1/2} (P_{\mathrm{u}} (H_z^{\mathrm{PP}} - \epsilon_{\mathrm{F}}^0) P_{\mathrm{u}})^{1/2} A_{\mathrm{uf}}\right)\right|, \end{aligned}$$

where $(H_z^{\mathrm{PP}} - \epsilon_{\mathrm{F}}^0)\big|_{\mathcal{H}_{\mathrm{u}}}^{-1/2}$ denotes the bounded operator on $L^2(\mathbb{R}^3)$ block-diagonal in the decomposition (3.71) identically equal to zero on $\mathcal{H}_{\mathrm{f}} \oplus \mathcal{H}_{\mathrm{p}}$ and equal to the inverse square root of the invertible positive operator $(H_z^{\mathrm{PP}} - \epsilon_{\mathrm{F}}^0)\big|_{\mathcal{H}_{\mathrm{u}}}$ on $\mathcal{H}_{\mathrm{u}}$. As the space $\mathcal{A}_{\mathrm{uf}}$ consists of finite-rank operators with rank lower or equal to N_{f}, the operator and trace norms are equivalent on this space, and we therefore obtain

$$\begin{aligned} \forall A \in \mathcal{A}, \quad |\mathrm{Tr}\,((P_{\mathrm{u}} W P_{\mathrm{f}})^* A_{uf})| &\leq (E_+ - \epsilon_{z,\mathrm{F}}^0)^{-1/2} \|P_f W\|\, \|A_{\mathrm{uf}}\|_{\mathcal{A}_{\mathrm{uf}}} \\ &\leq (E_+ - \epsilon_{z,\mathrm{F}}^0)^{-1/2} \max_{1 \leq n \leq N_{\mathrm{f}}} \|W \phi_n\|_{L^2}\, \|A_{\mathrm{uf}}\|_{\mathcal{A}_{\mathrm{uf}}}, \end{aligned}$$

where $(\phi_n)_{1 \leq n \leq N_{\mathrm{f}}}$ is an orthonormal basis of $\mathcal{H}_{\mathrm{f}}$. Similar arguments applied to the other components of $\zeta(W)$ lead to

$$\forall W \in C^\infty_{\mathrm{c}}(\mathbb{R}^3), \quad \|\zeta(W)\|_{\mathcal{A}'} \leq C_M \max_{0 \leq l \leq l_z,\, -l \leq m \leq l} \|W \widetilde{\phi}_{z,l}^m\|_{L^2}.$$

Using (3.70), we deduce from the above inequality that

$$\forall W \in C^\infty_{\mathrm{c}}(\mathbb{R}^3), \quad \|\zeta(W)\|_{\mathcal{A}'} \leq C_M \|W\|_{L^2_{\mathrm{w}}}.$$

As ζ is continuous from $\mathcal{C}'$ to $\mathcal{A}'$ (see [23]), we also have

$$\forall W \in C^\infty_{\rm c}(\mathbb{R}^3), \quad \|\zeta(W)\|_{\mathcal{A}'} \leq C_M \|W\|_{\mathcal{C}'+L^2_{\rm w}}. \tag{3.72}$$

The space $C^\infty_{\rm c}(\mathbb{R}^3)$ being dense in $\mathcal{C}'+L^2_{\rm w}$, we obtain that the linear map ζ can be extended in a unique way to a continuous linear map from $\mathcal{C}'+L^2_{\rm w}$ to $\mathcal{A}'$.

Let us now consider a sequence $(V^{\rm PP}_{z,k})_{k\in\mathbb{N}}$ of elements of $\mathcal{M}_{z,\Delta E,r_{\rm c},s}$ which weakly converges to some $V^{\rm PP}_z$ in $\mathcal{M}_{z,\Delta E,r_{\rm c},s}$. As $V_{z,{\rm loc},k}$ coincides with $-\frac{z}{|\cdot|}+\rho^0_{z,{\rm c}}\star|\cdot|^{-1}$ outside $B_{r_{\rm c}}$, we obtain that $(V^{\rm PP}_{z,k})_{k\in\mathbb{N}}$ converges to $V^{\rm PP}_z$ strongly in $\mathcal{M}_{z,\Delta E,r_{\rm c},s/2}$. To prove the compactness of the mapping $\mathcal{M}_{z,\Delta E,r_{\rm c},s} \ni V^{\rm PP}_z \mapsto \widetilde{\gamma}^{(1)}_{W^{\rm Stark}}(V^{\rm PP}_z) \in \mathfrak{S}_{1,1}$, it is therefore sufficient to show that the mapping $V^{\rm PP}_z \mapsto \widetilde{\gamma}^{(1)}_{W^{\rm Stark}}(V^{\rm PP})$ is strongly continuous from $\mathcal{M}_{z,\Delta E,r_{\rm c},s}$ to $\mathfrak{S}_{1,1}$ for any $s>0$. Let us therefore consider a sequence $(V^{\rm PP}_{z,k})_{k\in\mathbb{N}}$ of elements of $\mathcal{M}_{z,\Delta E,r_{\rm c},s}$ which strongly converges to some $V^{\rm PP}_z$ in $\mathcal{M}_{z,\Delta E,r_{\rm c},s}$ and $M\in\mathbb{R}_+$ such that

$$\sup_{k\in\mathbb{N}} \|V^{\rm PP}_{z,k} - V_{\rm ref}\|_{X_{z,\Delta E,r_{\rm c},s}} \leq M.$$

Using [23, Eqs. (42)-(43)], (3.72), the bound

$$\|H^{\rm PP}_{z,k}(1-\Delta)^{-1}\| \leq C_M,$$

and the fact that there exists $0<c_M\leq C_M<+\infty$ such that

$$\forall (A,A')\in\mathcal{A}\times\mathcal{A}, \quad \langle\Theta(A),A\rangle \geq c_M\|A\|^2_{\mathcal{A}} \quad \text{and} \quad \langle\Theta(A),A'\rangle \leq C_M\|A\|_{\mathcal{A}}\|A'\|_{\mathcal{A}},$$

where the bilinear form Θ is defined in [23, Eq. (59)], we obtain that

$$\sup_{k\in\mathbb{N}} \|\widetilde{\gamma}^{(1)}_W(V^{\rm PP}_{z,k})\|_{\mathfrak{S}_{1,1}} \leq C_M\|W\|_{\mathcal{C}'+L^2_{\rm w}}. \tag{3.73}$$

Let $\varepsilon>0$ and $W\in C^\infty_{\rm c}(\mathbb{R}^3)$ be such that $\|W-W^{\rm Stark}\|_{\mathcal{C}'+L^2_{\rm w}}\leq\varepsilon/(3C_M)$, where C_M is the constant in (3.73). By the triangular inequality,

$$\begin{aligned}\|\widetilde{\gamma}^{(1)}_{W^{\rm Stark}}(V^{\rm PP}_{z,k}) - \widetilde{\gamma}^{(1)}_{W^{\rm Stark}}(V^{\rm PP}_z)\|_{\mathfrak{S}_{1,1}} &\leq \frac{2\varepsilon}{3} + \|\widetilde{\gamma}^{(1)}_W(V^{\rm PP}_{z,k}) - \widetilde{\gamma}^{(1)}_W(V^{\rm PP}_z)\|_{\mathfrak{S}_{1,1}} \\ &\leq \frac{2\varepsilon}{3} + \left\| \lim_{\beta\to0} \beta^{-1}\left(\widetilde{\gamma}_{V^{\rm PP}_{z,k}-V^{\rm PP}_z,\beta W}(V^{\rm PP}_z) - \widetilde{\gamma}_{0,\beta W}(V^{\rm PP}_z)\right)\right\|_{\mathfrak{S}_{1,1}}.\end{aligned}$$

We then infer from the analyticity properties of the mapping $(v,W)\mapsto\widetilde{\gamma}_{v,W}(V^{\rm PP})$ (cf. Proposition 33) that for k large enough, the second term of the right-hand side is lower than $\varepsilon/3$. Therefore, the mapping $V^{\rm PP}_z\mapsto\widetilde{\gamma}^{(1)}_{W^{\rm Stark}}(V^{\rm PP}_z)$ is strongly continuous from $\mathcal{M}_{z,\Delta E,r_{\rm c},s}$ to $\mathfrak{S}_{1,1}$.

3.5.8 Proof of Theorem 35

Let $(V^{\rm PP}_{z,k})_{k\in\mathbb{N}}$ be a minimizing sequence for (3.43). As $\alpha>0$ and $J_{\rm t}$ is bounded below, the sequence $(W^{\rm PP}_{z,k})_{k\in\mathbb{N}}$ is bounded for the norm $\|\cdot\|_{H^s}$ defined in (3.42). As $W^{\rm PP}_{z,k}$ coincides with $W^{\rm AA}_z$ outside $B_{r_{\rm c}}$, we can assume, without loss of generality, that $(W^{\rm PP}_{z,k})_{k\in\mathbb{N}}$ converges

to some $W_z^{\rm PP} = W_{z,\rm loc}^{\rm PP} + \sum_{l=0}^{l_z} P_l V_{z,l} P_l$, weakly for the norm $\|\cdot\|_{H^s}$, and strongly for the norm $\|\cdot\|_{H^{s-\eta}}$ for any $\eta > 0$. We then have

$$\frac{1}{2}\|W_z^{\rm PP}\|_{H^s}^2 \leq \liminf_{k\to\infty} J_{\rm s}(V_{z,k}^{\rm PP}). \tag{3.74}$$

Reasoning as in the proof of Theorem 31, we obtain that the ground state density $\widetilde{\rho}_k$ of

$$\inf\left\{ {\rm Tr}\left(\left(-\frac{1}{2}\Delta + V_{z,k}^{\rm PP}\right)\widetilde{\gamma}\right) + \frac{1}{2}D\left(\rho_{\widetilde{\gamma}}, \rho_{\widetilde{\gamma}}\right),\ \widetilde{\gamma} \in \mathcal{K}_{N_{z,\rm v}} \right\}$$

converges, when k goes to infinity, to some $\widetilde{\rho}$ in $H^s(\mathbb{R}^3)$, which is in fact the ground state density associated with the self-consistent pseudopotential $W_z^{\rm PP}$. This implies that $V_{z,{\rm loc},k}^{\rm PP} = W_{z,{\rm loc},k}^{\rm PP} - \widetilde{\rho}_k \star |\cdot|^{-1}$ weakly converges to $V_{z,\rm loc}^{\rm PP} := W_{z,\rm loc}^{\rm PP} - \widetilde{\rho}\star|\cdot|^{-1}$ in $H^s_{\rm loc}(\mathbb{R}^3)$. Therefore, $(V_{z,k}^{\rm PP})_{k\in\mathbb{N}}$ weakly converges in $X_{z,\Delta E,r_{\rm c},s}$ to $V_z^{\rm PP} = V_{z,\rm loc}^{\rm PP} + \sum_{l=0}^{l_z} P_l V_{z,l} P_l$, which belongs to $\mathcal{M}_{z,\Delta E,r_{\rm c},s}$ by virtue of Theorem 31, and $W_z^{\rm PP}$ is the self-consistent pseudopotential associated with $V_z^{\rm PP}$. Using (3.74) and the weak lower-semicontinuity property of $J_{\rm t}$, we finally obtain that

$$J(V_z^{\rm PP}) \leq \liminf_{k\to\infty} J(V_{z,k}^{\rm PP}),$$

which implies that $V_z^{\rm PP}$ is a minimizer to (3.43).

3.5.9 Proof of Lemma 36

Let $(V_{z,k}^{\rm PP})_{k\in\mathbb{N}}$ be a sequence of elements of $\mathcal{M}_{z,\Delta E,{\rm c},s}$ weakly converging to $V_z^{\rm PP}$ in $\mathcal{X}_{z,\Delta E,{\rm c},s}$. By Theorem 31, $V_z^{\rm PP} \in \mathcal{M}_{z,\Delta E,r_{\rm c},s}$ and by Theorem 34, the sequence $(\widetilde{\gamma}^{(1)}_{W^{\rm Stark}}(V_{z,k}^{\rm PP}))_{k\in\mathbb{N}}$ strongly converges to $\widetilde{\gamma}^{(1)}_{W^{\rm Stark}}(V_z^{\rm PP})$ in $\mathfrak{S}_{1,1}$. Consequently, $(\widetilde{\rho}^{(1)}_{W^{\rm Stark}}(V_{z,k}^{\rm PP}))_{k\in\mathbb{N}}$ converges to $\widetilde{\rho}^{(1)}_{W^{\rm Stark}}(V_z^{\rm PP})$ strongly in $L^{6/5}(\mathbb{R}^3)$, which implies that $(\mathbb{1}_{\mathbb{R}^3\setminus B_{r_{\rm c}}}\widetilde{\rho}^{(1)}_{W^{\rm Stark}}(V_{z,k}^{\rm PP}))_{k\in\mathbb{N}}$ converges to $\mathbb{1}_{\mathbb{R}^3\setminus B_{r_{\rm c}}}\widetilde{\rho}^{(1)}_{W^{\rm Stark}}(V_z^{\rm PP})$ in $L^{6/5}(\mathbb{R}^3)$, hence in $\mathcal{C}$, which implies that the sequence of non-negative real-numbers $(J_{\rm t}^{\rm Stark}(V_{z,k}^{\rm PP}))_{k\in\mathbb{N}}$ converges to $J_{\rm t}^{\rm Stark}(V_z^{\rm PP})$.

Chapter 4

A numerical study of the Kohn-Sham ground states of atoms

This chapter is concerned with the numerical simulation of the Kohn-Sham model for atoms subjected to cylindrically-symmetric external potentials. We deal with both the Hartree model and the Xα model. We start by presenting these models with and without perturbation and by recalling some well-known theoretical results we need. The variational approximation of the model and the construction of appropriate discretization spaces (using $\mathbb{P}_4$-finite elements) are detailed together with the algorithm to solve the discretized Kohn-Sham equations used in our code. The last section is devoted for the numerical results we have obtained: first, we report the computed energy levels of all the atoms of the four first rows of the periodic table. Interestingly, we observe accidentally degeneracies between s and d shells or between p and d shells at the Fermi level of some atoms. Second, we consider the case of an atom subjected to a uniform electric-field. We plot the response of the density of the boron atom for various magnitudes of the electric field computed numerically in a large ball with Dirichlet boundary conditions, and we check that, in the limit of small electric fields, it is equivalent to the first-order perturbation of the ground state density. Some technical details are gathered in an appendix at the end of the chapter.

4.1 Introduction

This chapter is concerned with the numerical computation of the extended Kohn-Sham ground states of atoms for the reduced Hartree-Fock (rHF, also called Hartree) and LDA (local density approximation) models. We consider the case of an isolated atom, as well as the case of an atom subjected to cylindrically symmetric external potential. We notably have in mind Stark potentials, that are potentials of the form $W(\mathbf{r}) = -\mathcal{E} \cdot \mathbf{r}$ generated by a uniform electric field $\mathcal{E} \neq 0$.

We first propose a new method to accurately solve the extended Kohn-Sham problem for cylindrically symmetric systems, using spherical coordinates and a separation of variables. This approach is based on the fact that, for such systems, the Kohn-Sham Hamiltonian commutes with $L_{\mathbf{z}}$, the $\mathbf{z}$-component of the angular momentum operator, $\mathbf{z}$ denoting the symmetry axis of the system. We obtain in this way a family of 2D elliptic eigenvalue problems in the r and θ variables, index by the eigenvalue $m \in \mathbb{Z}$ of $L_{\mathbf{z}}$, all these problems being coupled together through the self-consistent density. To discretize the 2D eigenvalue problems, we use harmonic polynomials in θ (or in other words, spherical harmonics Y_l^0, which only depend on θ) to discretize along the angular variable, and $\mathbb{P}_4$ finite element methods to discretize along the radial variable $r \in [0, L_e]$. We then apply this approach to study numerically two kind of systems.

First, we provide accurate approximations of the extended Kohn-Sham ground states of all atoms of the first four rows of the periodic table. These results allow us to test numerically the assumptions on the negative spectra of atomic rHF Hamiltonians that we use in our theoretical works on density functional perturbation theory [23] and norm-conserving semilocal pseudopotentials [25]. We show in particular that for most atoms of the first four rows of the periodic table, the Fermi level is negative and is not an accidentally degenerate eigenvalue of the rHF Hamiltonian, and that there seems to be no unoccupied orbitals with negative energies. On the other hand, for a few atoms, the Fermi level seems to be an accidentally degenerate eigenvalue (for example the $5s$ and $4d$ states being degenerate).

Second, we study an atom subjected to uniform electric field (Stark effect). In this case, the system has no ground state (the Kohn-Sham energy functional is not bounded below), but density functional perturbation theory (see [23, 25] for a mathematical analysis) can be used to compute the polarization of the electronic cloud caused by the external electric field. The polarized electronic state is not a steady state, but a resonant state, and the smaller the electric field, the longer its life time. Another way to compute the polarization of the electronic cloud is to compute the ground state for a small enough electric field in a basis set consisting of functions decaying fast enough at infinity for the electrons to stay close to the nuclei. The Gaussian basis functions commonly used in quantum chemistry satisfy this decay property. However, it is not easy to obtain very accurate results with Gaussian basis sets, since they are not systematically improvable (over-completeness issues). Here we consider instead basis functions supported in a ball B_{L_e}, where L_e is a numerical parameter chosen large enough to obtain accurate results and small enough to prevent electrons from escaping to infinity (for a given, small, value of the external electric field $\mathcal{E}$). We study the ground state energy and density as functions of the cut-off radius L_e, and observe that for a given, small enough, uniform electric field, there is a plateau $[L_{e,\min}, L_{e,\max}]$ on which

these quantity hardly vary. For $L_e < L_{e,\min}$, the simulated system is too much confined, which artificially increases its energy, while for $L_e > L_{e,\max}$, a noticeable amount of charge accumulates at the boundary of the simulation domain, in the direction of $\mathcal{E}$ (where the potential energy is very negative). On the other hand, for $L_{e,\min} \leq L_e \leq L_{e,\max}$, the simulation provides a fairly accurate approximation of the polarization energy and of the polarized density.

The chapter is organized as follows. In Section 4.2, we recall the mathematical formulation of the extended Kohn-Sham model, and some theoretical results about the rHF and LDA ground states of isolated atoms and of atoms subjected to an external cylindrically symmetric potential. In Section 4.3, we describe the discretization method and the algorithms used in this work to compute the extended Kohn-Sham ground states of atoms subjected to cylindrically symmetric external potentials. Some numerical results are presented in Section 4.4. Lastly, some details about the practical implementation of our methods are provided in Appendix.

4.2 Modeling

In this article, we consider a molecular system consisting of single nucleus of atomic charge $z \in \mathbb{N}^*$ and of N electrons. For $N = z$, this system is the neutral atom with nuclear charge z, which we call atom z for convenience.

4.2.1 Kohn-Sham models for atoms

In the framework of the (extended) Kohn-Sham model [28], the ground state energy of a system with one nucleus with charge z and N electrons is obtained by minimizing an energy functional of the form

$$E_{z,N}(\gamma) := \mathrm{Tr}\left(-\frac{1}{2}\Delta\gamma\right) - z\int_{\mathbb{R}^3}\frac{\rho_\gamma}{|\cdot|} + \frac{1}{2}D(\rho_\gamma,\rho_\gamma) + E_{\mathrm{xc}}(\rho_\gamma) \tag{4.1}$$

over the set

$$\mathcal{K}_N := \left\{\gamma \in \mathcal{S}(L^2(\mathbb{R}^3)) \mid 0 \leq \gamma \leq 2,\ \mathrm{Tr}\,(\gamma) = N,\ \mathrm{Tr}\,(-\Delta\gamma) < \infty\right\},$$

where $\mathcal{S}(L^2(\mathbb{R}^3))$ is the space of the self-adjoint operators on $L^2(\mathbb{R}^3)$ and $\mathrm{Tr}\,(-\Delta\gamma) := \mathrm{Tr}\,(|\nabla|\gamma|\nabla|)$. Note that, $\mathcal{K}_N$ is a closed convex subset of the space $\mathfrak{S}_{1,1}$ defined by

$$\mathfrak{S}_{1,1} := \{T \in \mathfrak{S}_1 \mid |\nabla|T|\nabla| \in \mathfrak{S}_1\},$$

endowed with norm

$$\|T\|_{\mathfrak{S}_{1,1}} := \|T\|_{\mathfrak{S}_1} + \||\nabla\,|T|\nabla|\,\|_{\mathfrak{S}_1}.$$

The function $-\frac{z}{|\cdot|}$ is the attraction potential induced on the electrons by the nucleus, and ρ_γ is the density associated with the one-body density matrix γ. For $\gamma \in \mathcal{K}_N$, we have

$$\rho_\gamma \geq 0, \quad \int_{\mathbb{R}^3}\rho_\gamma = N, \quad \int_{\mathbb{R}^3}|\nabla\sqrt{\rho_\gamma}|^2 \leq \mathrm{Tr}\,(-\Delta\gamma) < \infty.$$

The last result is the Hoffmann-Ostenhof inequality [52]. Therefore $\sqrt{\rho_\gamma} \in H^1(\mathbb{R}^3)$, and in particular, $\rho_\gamma \in L^1(\mathbb{R}^3) \cap L^3(\mathbb{R}^3)$. For $\rho \in L^{\frac{6}{5}}(\mathbb{R}^3)$, $D(\rho,\rho)$ is equal to $\int_{\mathbb{R}^3} V^{\mathrm{H}}(\rho)\rho$, where V^{H} is the Coulomb, also called Hartree, potential generated by ρ:

$$V^{\mathrm{H}}(\rho) = \rho \star |\cdot|^{-1}.$$

Recall that V^{H} can be seen as a unitary operator from the Coulomb space $\mathcal{C}$ to its dual $\mathcal{C}'$, where

$$\mathcal{C} := \left\{\rho \in \mathcal{S}'(\mathbb{R}^3) \,|\, \widehat{\rho} \in L^1_{\mathrm{loc}}(\mathbb{R}^3),\, |\cdot|^{-1}\widehat{\rho} \in L^2(\mathbb{R}^3)\right\}, \quad (\rho_1,\rho_2)_{\mathcal{C}} = 4\pi \int_{\mathbb{R}^3} \frac{\overline{\widehat{\rho_1}(\mathbf{k})}\widehat{\rho}_2(\mathbf{k})}{|\mathbf{k}|^2}\, d\mathbf{k}, \tag{4.2}$$

and

$$\mathcal{C}' := \left\{v \in L^6(\mathbb{R}^3) \mid \nabla v \in (L^2(\mathbb{R}^3))^3\right\}, \quad (v_1,v_2)_{\mathcal{C}'} = \frac{1}{4\pi}\int_{\mathbb{R}^3} \nabla v_1 \nabla v_2 = \frac{1}{4\pi}\int_{\mathbb{R}^3} |\mathbf{k}|^2 \overline{\widehat{v_1}(\mathbf{k})}\widehat{v}_2(\mathbf{k})\, d\mathbf{k}. \tag{4.3}$$

The term E_{xc} is the exchange-correlation energy. We will restrict ourselves to two kinds of Kohn-Sham models: the rHF model, for which the exchange-correlation energy is taken equal to zero

$$E_{\mathrm{xc}}^{\mathrm{rHF}} = 0,$$

and the Khon-Sham LDA (local density approximation) model, for which the exchange-correlation energy has the form

$$E_{\mathrm{xc}}^{\mathrm{LDA}}(\rho) = \int_{\mathbb{R}^3} \epsilon_{\mathrm{xc}}(\rho(r))\, dr,$$

where ϵ_{xc} is the sum of the exchange and correlation energy densities of the homogeneous electron gas. As the function $\epsilon_{\mathrm{xc}} : \mathbb{R}_+ \to \mathbb{R}$ is not explicitly known, it is approximated in practice by an explicit function, still denoted by ϵ_{xc} for simplicity. We assume here that the approximate function ϵ_{xc} is a C^1 function from $\mathbb{R}_+$ into $\mathbb{R}_-$, twice differentiable on $\mathbb{R}_+^*$ and obeying the following conditions

$$\epsilon_{\mathrm{xc}}(0) = 0, \quad \epsilon'_{\mathrm{xc}}(0) \leq 0, \tag{4.4}$$

$$\exists 0 < \beta_- \leq \beta_+ < \frac{3}{2} \quad \text{s.t} \quad \sup_{\rho\in\mathbb{R}_+} \frac{|\epsilon'_{\mathrm{xc}}(\rho)|}{\rho^{\beta_-} + \rho^{\beta_+}} < \infty, \tag{4.5}$$

$$\exists 1 \leq \alpha < \frac{3}{2} \quad \text{s.t} \quad \limsup_{\rho\to 0_+} \frac{\epsilon_{\mathrm{xc}}(\rho)}{\rho^\alpha} < 0, \tag{4.6}$$

$$\exists \lambda > -1 \quad \text{s.t} \quad \epsilon''_{\mathrm{xc}}(\rho) \underset{0}{\sim} c\rho^\lambda. \tag{4.7}$$

Note that these properties are satisfied by the exact function ϵ_{xc}.

To avoid ambiguity, for any z and N in $\mathbb{R}_+^*$, we denote by

$$\mathcal{I}_{z,N}^{\mathrm{rHF}} := \inf\left\{E_{z,N}^{\mathrm{rHF}}(\gamma),\, \gamma \in \mathcal{K}_N\right\}, \tag{4.8}$$

where

$$E^{\mathrm{rHF}}_{z,N}(\gamma) := \mathrm{Tr}\left(-\frac{1}{2}\Delta\gamma\right) - z\int_{\mathbb{R}^3}\frac{\rho_\gamma}{|\cdot|} + \frac{1}{2}D(\rho_\gamma,\rho_\gamma),$$

and

$$\mathcal{I}^{\mathrm{LDA}}_{z,N} := \inf\left\{E^{\mathrm{LDA}}_{z,N}(\gamma),\, \gamma\in\mathcal{K}_N\right\}, \tag{4.9}$$

where

$$E^{\mathrm{LDA}}_{z,N}(\gamma) := \mathrm{Tr}\left(-\frac{1}{2}\Delta\gamma\right) - z\int_{\mathbb{R}^3}\frac{\rho_\gamma}{|\cdot|} + \frac{1}{2}D(\rho_\gamma,\rho_\gamma) + E^{\mathrm{LDA}}_{\mathrm{xc}}(\rho_\gamma).$$

We recall the following two theorems which insure the existence of ground states for neutral atoms and positive ions.

Theorem 40 (Ground state for the rHF model [23, 81])**.** *Let $z\in\mathbb{R}^*_+$ and $N\leq z$. Then the minimization problem (4.8) has a ground state $\gamma^{0,\mathrm{rHF}}_{z,N}$, and all the ground states share the same density $\rho^{0,\mathrm{rHF}}_{z,N}$. The mean-field Hamiltonian*

$$H^{0,\mathrm{rHF}}_{z,N} := -\frac{1}{2}\Delta - \frac{z}{|\cdot|} + V^{\mathrm{H}}(\rho^{0,\mathrm{rHF}}_{z,N}),$$

is a bounded below self-adjoint operator on $L^2(\mathbb{R}^3)$, $\sigma_{\mathrm{ess}}(H^{0,\mathrm{rHF}}_{z,N}) = \mathbb{R}_+$, and the ground state $\gamma^{0,\mathrm{rHF}}_{z,N}$ is of the form

$$\gamma^{0,\mathrm{rHF}}_{z,N} = 2\mathbb{1}_{(-\infty,\epsilon^{0,\mathrm{rHF}}_{z,N,\mathrm{F}})}(H^{0,\mathrm{rHF}}_{z,N}) + \delta^{0,\mathrm{rHF}}_{z,N},$$

where $\epsilon^{0,\mathrm{rHF}}_{z,N,\mathrm{F}}\leq 0$ is the Fermi level, $0\leq\delta^{0,\mathrm{rHF}}_{z,N}\leq 2$ and $\mathrm{Ran}(\delta^{0,\mathrm{rHF}}_{z,N})\subset\mathrm{Ker}(H^{0,\mathrm{rHF}}_{z,N}-\epsilon^{0,\mathrm{rHF}}_{z,N,\mathrm{F}})$. If $\epsilon^{0,\mathrm{rHF}}_{z,N,\mathrm{F}}$ is negative and is not an accidentally degenerate eigenvalue of $H^{0,\mathrm{rHF}}_{z,N}$, then $\gamma^{0,\mathrm{rHF}}_{z,N}$ is unique.

Theorem 41 (Ground state for the LDA model [1])**.** *Let $z\in\mathbb{R}^*_+$ and $N\leq z$. Suppose that (4.4)-(4.6) hold. Then the minimization problem (4.9) has a ground state $\gamma^{0,\mathrm{LDA}}_{z,N}$. In addition, $\gamma^{0,\mathrm{LDA}}_{z,N}$ satisfies the self-consistent field equation*

$$\gamma^{0,\mathrm{LDA}}_{z,N} = 2\mathbb{1}_{(-\infty,\epsilon^{0,\mathrm{LDA}}_{z,N,\mathrm{F}})}(H^{0,\mathrm{LDA}}_{z,N}) + \delta^{0,\mathrm{LDA}}_{z,N}, \tag{4.10}$$

where $\epsilon^{0,\mathrm{LDA}}_{z,N,\mathrm{F}}\leq 0$ is the Fermi level, $0\leq\delta^{0,\mathrm{LDA}}_{z,N}\leq 2$, $\mathrm{Ran}(\delta^{0,\mathrm{LDA}}_{z,N})\subset\mathrm{Ker}(H^{0,\mathrm{LDA}}_{z,N}-\epsilon^{0,\mathrm{LDA}}_{z,N,\mathrm{F}})$ and the mean-field Hamiltonian

$$H^{0,\mathrm{LDA}}_{z,N} := -\frac{1}{2}\Delta - \frac{z}{|\cdot|} + V^{\mathrm{H}}(\rho^{0,\mathrm{LDA}}_{z,N}) + v_{\mathrm{xc}}(\rho^{0,\mathrm{LDA}}_{z,N}),$$

where $\rho^{0,\mathrm{LDA}}_{z,N} = \rho_{\gamma^{0,\mathrm{LDA}}_{z,N}}$ and $v_{\mathrm{xc}}(\rho) = \frac{d\epsilon_{\mathrm{xc}}}{d\rho}(\rho)$, is a bounded below self-adjoint operator on $L^2(\mathbb{R}^3)$ and $\sigma_{\mathrm{ess}}(H^{0,\mathrm{LDA}}_{z,N}) = \mathbb{R}_+$.

4.2.2 Density function perturbation theory

We now examine the response of the ground state density matrix when an additional external potential βW is turned on. The energy functional to be minimized over $\mathcal{K}_N$ now reads

$$\widetilde{E}^{\mathrm{rHF/LDA}}_{z,N}(\gamma, \beta W) := E^{\mathrm{rHF/LDA}}_{z,N}(\gamma) + \int_{\mathbb{R}^3} \beta W \rho_\gamma, \tag{4.11}$$

and is well-defined for any $\gamma \in \mathcal{K}_N$, $W \in \mathcal{C}'$ and $\beta \in \mathbb{R}$. The parameter β is called the coupling constant in quantum mechanics. Denote by

$$\widetilde{\mathcal{I}}^{\mathrm{rHF/LDA}}_{z,N}(\beta W) := \inf \left\{ \widetilde{E}^{\mathrm{rHF/LDA}}_{z,N}(\gamma, \beta W),\, \gamma \in \mathcal{K}_N \right\}. \tag{4.12}$$

The following theorem insures the existence of a perturbed ground state density matrix for perturbation potentials in $\mathcal{C}'$.

Theorem 42 (Existence of a perturbed minimizer [23])**.** *Let $z \in \mathbb{R}^*_+$, $N \leq z$, $W \in \mathcal{C}'$ and $\beta \in \mathbb{R}$, β small enough. In the rHF framework, problem (4.12) has a unique minimizer $\gamma^{\mathrm{rHF}}_{z,N,\beta W}$. The Hamiltonian*

$$H^{\mathrm{rHF}}_{z,N,\beta W} = -\frac{1}{2}\Delta - \frac{z}{|\cdot|} + V^{\mathrm{H}}(\rho^{\mathrm{rHF}}_{z,N,\beta W}) + \beta W, \tag{4.13}$$

where $\rho^{\mathrm{rHF}}_{z,N,\beta W} = \rho_{\gamma^{\mathrm{rHF}}_{z,N,\beta W}}$, is a bounded below self-adjoint operator on $L^2(\mathbb{R}^3)$ with form domain $H^1(\mathbb{R}^3)$ and $\sigma_{\mathrm{ess}}(H^{0,\mathrm{rHF}}_{z,N,\beta W}) = \mathbb{R}_+$. Moreover, $\gamma^{\mathrm{rHF}}_{z,N,\beta W}$ and $\rho^{\mathrm{rHF}}_{z,N,\beta W}$ are analytic in β, that is

$$\gamma^{\mathrm{rHF}}_{z,N,\beta W} = \sum_{k\geq 0} \beta^k \gamma^{(k),\mathrm{rHF}}_{z,N,W} \quad \text{and} \quad \rho^{\mathrm{rHF}}_{z,N,\beta W} = \sum_{k\geq 0} \beta^k \rho^{(k),\mathrm{rHF}}_{z,N,W},$$

the above series being normally convergent in $\mathfrak{S}_{1,1}$ and $\mathcal{C}$ respectively.

In the sequel, we will refer to $\gamma^{(k)}_{z,N,W}$ as the k-th order perturbation of the density matrix.

The unperturbed Hamiltonians $H^{0,\mathrm{rHF}}_{z,N}$ are self-adjoint operators on $L^2(\mathbb{R}^3)$ invariant with respect to rotations around the nucleus (assumed located at the origin). These operators are therefore block-diagonal in the decomposition of $L^2(\mathbb{R}^3)$ as the direct sum of the pairwise orthogonal subspaces $\mathcal{H}_l := \mathrm{Ker}(\mathbf{L}^2 - l(l+1))$:

$$L^2(\mathbb{R}^3) = \bigoplus_{l\in\mathbb{N}} \mathcal{H}_l, \tag{4.14}$$

where $\mathbf{L} = \mathbf{r} \times (-i\nabla)$ is the angular momentum operator. Since we are going to consider perturbation potentials which are not spherically symmetric, but only cylindrically symmetric, or in other words independent of the azimuthal angle φ in spherical coordinates, the $\mathcal{H}_l$'s are no longer invariant subspaces of the perturbed Hamiltonians. The appropriate decomposition of $L^2(\mathbb{R}^3)$ in invariant subspaces for Hamiltonians $H^{\mathrm{rHF}}_{z,N,\beta W}$ with W cylindrically symmetric, is the following: for $m \in \mathbb{Z}$, we set

$$\mathcal{H}^m := \mathrm{Ker}(L_{\mathbf{z}} - m),$$

where $L_{\mathbf{z}}$ is the $\mathbf{z}$-component of the angular momentum operator $\mathbf{L}$ ($L_{\mathbf{z}} = \mathbf{L}.\mathbf{e}_{\mathbf{z}}$).

Note that

$$\forall l \in \mathbb{N}, \quad \mathcal{H}_l = \left\{ \phi \in L^2(\mathbb{R}^3), \quad \text{s.t} \quad \phi(r,\theta,\varphi) = \sum_{-l \leq m \leq l} R^m(r) Y_l^m(\theta,\varphi) \right\},$$

and

$$\forall m \in \mathbb{Z}, \quad \mathcal{H}^m = \left\{ \phi \in L^2(\mathbb{R}^3), \quad \text{s.t} \quad \phi(r,\theta,\varphi) = \sum_{l \geq |m|} R_l(r) Y_l^m(\theta,\varphi) \right\},$$

where Y_l^m are the spherical harmonics, the joint eigenfunctions of the Laplace-Beltrami operator Δ_S and the generator of rotations about the azimuthal axis $\mathcal{L}_{\mathbf{z}}$ on $L^2(\mathbb{S}^2)$, where $\mathbb{S}^2$ is the unit sphere of $\mathbb{R}^3$. More precisely, we have

$$-\Delta_S Y_l^m = l(l+1) Y_l^m \quad \text{and} \quad \mathcal{L}_{\mathbf{z}} Y_l^m = m Y_l^m,$$

where, in spherical coordinates,

$$\Delta_S = \frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial}{\partial\theta} \right) + \frac{1}{\sin^2(\theta)} \frac{\partial^2}{\partial\varphi^2} \quad \text{and} \quad \mathcal{L}_{\mathbf{z}} = -i \frac{\partial}{\partial\varphi}.$$

These functions are orthonormal, in the following sense:

$$\int_{\mathbb{S}^2} Y_l^m (Y_{l'}^{m'})^* = \int_{\theta=0}^{\pi} \int_{\varphi=0}^{2\pi} Y_l^m(\theta,\varphi) \left(Y_{l'}^{m'}(\theta,\varphi) \right)^* \sin\theta \, d\theta \, d\varphi = \delta_{ll'} \delta_{mm'}, \tag{4.15}$$

where δ_{ij} is the Kronecker symbol and $(Y_l^m)^* = (-1)^m Y_l^{-m}$ is the complex conjugate of Y_l^m.

We also define

$$\mathcal{V}^m := \mathcal{H}^m \cap H^1(\mathbb{R}^3),$$

so that $L^2(\mathbb{R}^3)$ and $H^1(\mathbb{R}^3)$ are decomposed as the following direct sums:

$$L^2(\mathbb{R}^3) = \bigoplus_{m \in \mathbb{Z}} \mathcal{H}^m \quad \text{and} \quad H^1(\mathbb{R}^3) = \bigoplus_{m \in \mathbb{Z}} \mathcal{V}^m, \tag{4.16}$$

each $\mathcal{H}^m$ being $H^{\mathrm{rHF}}_{z,N,\beta W}$-stable (in the sense of unbounded operators) for W cylindrically symmetric. This is due to the fact that, for W being cylindrically symmetric, the operator $H^{\mathrm{rHF}}_{z,N,\beta W}$ commutes with $L_{\mathbf{z}}$. Note that $\sigma(H^{\mathrm{rHF}}_{z,N,\beta W}) = \overline{\bigcup_{m \in \mathbb{Z}} \sigma\left(H^{\mathrm{rHF}}_{z,N,\beta W} | \mathcal{H}^m \right)}$. Same arguments hold true for $H^{\mathrm{LDA}}_{z,N,\beta W}$ under the assumption that the ground state density $\rho^{0,\mathrm{LDA}}_{z,N,\beta W}$ is cylindrically symmetric (which is the case whenever it is unique).

With the new decomposition defined in (4.16), the ground state density matrix $\gamma^{0,\mathrm{rHF/LDA}}_{z,N}$ can be written as

$$\gamma^{0,\mathrm{rHF/LDA}}_{z,N} = \sum_{(m,k)\,|\epsilon^0_{m,k} \leq \epsilon^{0,\mathrm{rHF/LDA}}_{z,N,\mathrm{F}}} n^{(0)}_{m,k} |\Phi^{(0)}_{m,k}\rangle\langle\Phi^{(0)}_{m,k}|, \tag{4.17}$$

where $\epsilon^0_{m,k}$ is the k-th negative eigenvalue of the Hamiltonian $H^{0,\mathrm{rHF/LDA}}_{z,N}$ in the subspace $\mathcal{H}^m$, $(\Phi^{(0)}_{m,k})$ is an L^2-orthonormal family of associated eigenvectors ($H^{0,\mathrm{rHF/LDA}}_{z,N}\Phi^{(0)}_{m,k} = \epsilon^0_{m,k}\Phi^{(0)}_{m,k}$, $(\Phi^{(0)}_{m,k}, \Phi^{(0)}_{m',k'})_{L^2} = \delta_{mm'}\delta_{kk'}$), while $0 \leq n^{(0)}_{m,k} \leq 2$ is the occupation number of the orbital $\Phi^{(0)}_{m,k}$. Let us denote by

$$\mathcal{O}_{z,N} := \left\{(m,k) \in \mathbb{Z}\times\mathbb{N}^*|\ \epsilon^0_{m,k} \leq \epsilon^{0,\mathrm{rHF/LDA}}_{z,N,\mathrm{F}}\right\} \tag{4.18}$$

the set of indices (m,k) such that the eigenfunction associated to the k-th lowest eigenvalue (counting multiplicity) in the $\mathcal{V}^m$ subspace is an occupied orbital (i.e $n^{(0)}_{m,k} \neq 0$). By convention, we take $\epsilon^0_{m,k} = \min\sigma_{\mathrm{ess}}(H^{0,\mathrm{rHF/LDA}}_{z,N}|_{\mathcal{H}^m}) = 0$ if $H^{0,\mathrm{rHF/LDA}}_{z,N}|_{\mathcal{H}^m}$ has at most $(k-1)$ negative eigenvalues.

We are interested in the Stark potential

$$W_{\mathrm{Stark}}(\mathbf{r}) = -e_{\mathbf{z}}\cdot\mathbf{r}, \tag{4.19}$$

which does not belong to $\mathcal{C}'$, and thus does not fall into the scope of Theorem 42. We therefore introduce the classes of perturbation potentials

$$\mathcal{W}_s := \left\{W \in \mathcal{H}^0_{\mathrm{loc}}|\quad \int_{\mathbb{R}^3}\frac{|W|^2}{(1+|.|^2)^s} < \infty\right\},$$

where $\mathcal{H}^0_{\mathrm{loc}} := \mathcal{H}^0 \cap L^2_{\mathrm{loc}}(\mathbb{R}^3)$, which contain the Stark potential W_{Stark} whenever $s > 5/2$. For $W \in \mathcal{W}_s \setminus \mathcal{C}'$, the energy functional (4.11) is not necessarily bounded below on $\mathcal{K}_N$ for $\beta \neq 0$. Thus the solution of (4.12) may not exist. This is the case for the Stark potential W_{Stark}. However, the k-th order perturbation may exist, as this is the case when the linear Schrödinger operator of the hydrogen atom is perturbed by the Stark potential W_{Stark} (see e.g [69]). The following theorem ensures the existence of the first order perturbation of the density matrix.

Theorem 43 (First order perturbation [25])**.** *Let $z \in \mathbb{R}^*_+$, $0 < N \leq z$, such that $\epsilon^{0,\mathrm{rHF}}_{z,N,\mathrm{F}} < 0$,[1] $s \in \mathbb{R}$ and $W \in \mathcal{W}_s$. In the rHF framework, the first order perturbation of the density matrix $\gamma^{(1),\mathrm{rHF}}_{z,N,W}$ is well defined in $\mathfrak{S}_{1,1}$.*

4.3 Numerical method

In this section, we will present the discretization method and the algorithms used to calculate numerically the ground state density matrices for (4.8), (4.9) and (4.12) for cylindrically symmetric perturbation potentials W, together with the minimum energy and the lowest eigenvalues of the associated Kohn-Sham operator. From now on, we make the assumption that the ground state density of (4.12), if it exists, is cylindrically symmetric which is always the case for the rHF model. Using spherical coordinates, we can write

$$W(r,\theta) = \sum_{l=0}^{+\infty} W_l(r)Y^0_l(\theta) \in \mathcal{H}^0$$

[1] Note that, $\epsilon^{0,\mathrm{rHF}}_{z,N,\mathrm{F}} < 0$ whenever $0 < N < z$ (see e.g. [81]).

(since Y_l^0 is independent of φ, we use the notation $Y_l^0(\theta)$ instead of $Y_l^0(\theta,\varphi)$). As the ground state density $\rho_{z,N,\beta W}$ is assumed to be cylindrically symmetric as well, one has

$$\rho_{z,N,\beta W}(r,\theta) = \sum_{l=0}^{+\infty} \rho_{z,N,\beta W,l}(r) Y_l^0(\theta).$$

The Hartree and the exchange-correlation potentials also have the same symmetry. For $\rho \in L^1(\mathbb{R}^3) \cap L^3(\mathbb{R}^3) \cap \mathcal{H}^0$, we have

$$V^{\mathrm{H}}(\rho)(r,\theta) = \sum_{l=0}^{+\infty} V_{\rho_l}^{\mathrm{H}}(r) Y_l^0(\theta), \quad \text{and} \quad v_{\mathrm{xc}}(\rho)(r,\theta) = \sum_{l=0}^{+\infty} (v_\rho^{\mathrm{xc}})_l(r) Y_l^0(\theta),$$

where, for each $l \geq 0$, $V_{\rho_l}^{\mathrm{H}}(r)$ solves the following differential equation

$$-\frac{1}{r}\frac{d^2}{dr^2}(rV_{\rho_l}^{\mathrm{H}}) + \frac{l(l+1)}{r^2} V_{\rho_l}^{\mathrm{H}} = 4\pi\rho_l$$

with boundary conditions

$$\lim_{r\to 0^+} rV_{\rho_l}^{\mathrm{H}}(r) = 0 \quad \text{and} \quad \lim_{r\to+\infty} rV_{\rho_l}^{\mathrm{H}}(r) = \left(4\pi \int_0^{+\infty} r^2 \rho_0(r)\, dr\right) \delta_{l0},$$

while $(v_\rho^{\mathrm{xc}})_l$ can be computed by projection on the spherical harmonics Y_l^0:

$$(v_\rho^{\mathrm{xc}})_l(r) = 2\pi \int_0^\pi v_{\mathrm{xc}}(\rho)(r,\theta) Y_l^0(\theta) \sin\theta d\theta.$$

4.3.1 Discretisation of the Kohn-Sham model

Recall that for $W \in \mathcal{W}_s$ and $\beta \neq 0$, the energy functional defined by (4.11) is not necessarily bounded below on $\mathcal{K}_N$, which implies in particular that (4.12) may have no ground state. Nevertheless, one can compute approximations of (4.12) in finite-dimensional spaces, provided that the basis functions decay fast enough at infinity. Let $N_h \in \mathbb{N}^*$ and $m_h \geq m_z^* := \max\{m |\, \exists k > 0;\, \epsilon_{m,k}^0 \leq \epsilon_{z,N,\mathrm{F}}^0\}$, and let $\{\mathcal{X}_i\}_{1\leq i\leq N_h} \in \left(H_0^1(0,+\infty)\right)^{N_h}$ be a free family of real-valued basis functions. We then introduce the finite-dimensional spaces

$$\mathcal{V}^{h,m} := \mathcal{V}^m \cap \mathrm{span}\left(\frac{\mathcal{X}_i(r)}{r} Y_l^m(\theta,\phi)\right)_{\substack{1\leq i\leq N_h \\ |m|\leq l\leq m_h}} \subset H^1(\mathbb{R}^3)$$

and

$$\mathcal{X}^h = \mathrm{span}(\mathcal{X}_1, \cdots, \mathcal{X}_{N_h}) \subset H_0^1(0,+\infty),$$

and the set

$$\mathcal{K}_{N,h} := \left\{ \gamma \in \mathcal{K}_N |\quad \gamma = \sum_{m=-m_h}^{m_h} \gamma^m, \quad \gamma^m \in \mathcal{S}(\mathcal{H}^m), \quad \text{and} \quad \mathrm{Ran}(\gamma^m) \subset \mathcal{V}^{h,m} \right\} \subset \mathcal{K}_N.$$

Variational approximation

A variational approximation of (4.12) is obtained by minimizing the energy functional (4.11) over the approximation set $\mathcal{K}_{N,h}$:

$$\widetilde{\mathcal{I}}^{\mathrm{rHF/LDA}}_{z,N,h}(\beta W) := \inf\left\{\widetilde{E}^{\mathrm{rHF/LDA}}_{z,N}(\gamma_h, \beta W),\ \gamma_h \in \mathcal{K}_{N,h}\right\}. \tag{4.20}$$

Any $\gamma_h \in \mathcal{K}_{N,h}$ can be written as

$$\gamma_h = \sum_{\substack{-m_h \le m \le m_h \\ 1 \le k \le (m_h - |m|+1)N_h}} n_{m,k} |\Phi_{h,m,k}\rangle\langle\Phi_{h,m,k}|, \tag{4.21}$$

with

$$\Phi_{h,m,k} \in \mathcal{V}^{h,m}, \quad \int_{\mathbb{R}^3} \Phi_{h,m,k}\Phi^*_{h,m,k'} = \delta_{kk'}, \quad 0 \le n_{m,k} \le 2, \quad \sum_{\substack{-m_h \le m \le m_h \\ 1 \le k \le (m_h - |m|+1)N_h}} n_{m,k} = N.$$

The functions $\Phi_{h,m,k}$ being in $\mathcal{V}^{h,m}$, they are of the form

$$\Phi_{h,m,k}(r,\theta,\varphi) = \sum_{l=|m|}^{m_h} \frac{u_l^{h,m,k}(r)}{r} Y_l^m(\theta,\varphi), \tag{4.22}$$

where for each $-m_h \le m \le m_h$, $1 \le k \le (m_h - |m|+1)N_h$ and $|m| \le l \le m_h$, $u_l^{h,m,k} \in \mathcal{X}^h$. Expanding the functions $u_l^{h,m,k}$ in the basis $(\mathcal{X}_i)_{1 \le i \le N_h}$ as

$$u_l^{h,m,k}(r) = \sum_{i=1}^{N_h} U_{i,l}^{m,k} \mathcal{X}_i(r), \tag{4.23}$$

and gathering the coefficients $U_{i,l}^{m,k}$ for fixed m and k in a rectangular matrix $U^{m,k} \in \mathbb{R}^{N_h \times (m_h - |m|+1)}$, any $\gamma_h \in \mathcal{K}_{N,h}$ can be represented via (4.21)-(4.23) by at least one element of the set

$$\mathcal{M}_{N,h} := \mathcal{U}_{N,h} \times \mathcal{N}_{N,h}, \tag{4.24}$$

where

$$\mathcal{U}_{N,h} := \left\{ (U^{m,k})_{\substack{-m_h \le m \le m_h \\ 1 \le k \le (m_h - |m|+1)N_h}} \mid U^{m,k} \in \mathbb{R}^{N_h \times (m_h - |m|+1)},\ \mathrm{Tr}\left([U^{m,k}]^T M_0 U^{m,k'}\right) = \delta_{kk'} \right\},$$

and

$$\mathcal{N}_{N,h} := \left\{ (n_{m,k})_{\substack{-m_h \le m \le m_h \\ 1 \le k \le (m_h - |m|+1)N_h}},\ 0 \le n_{m,1} \le \cdots \le n_{m,(m_h - |m|+1)N_h} \le 2,\ \sum_{\substack{-m_h \le m \le m_h \\ 1 \le k \le (m_h - |m|+1)N_h}} n_{m,k} = N \right\}.$$

The matrix M_0 appearing in the definition of $\mathcal{U}_{N,h}$ is the mass matrix defined by

$$[M_0]_{ij} = \int_0^{+\infty} \mathcal{X}_i \mathcal{X}_j,$$

and the constraints $\mathrm{Tr}\,([U^{m,k}]^T M_0 U^{m,k'}) = \delta_{kk'}$ come from the fact that

$$\int_{\mathbb{R}^3} \Phi_{h,m,k}\Phi^*_{h,m,k'} = \int_0^{+\infty}\int_{\mathbb{S}^2} \left(\sum_{l=|m|}^{m_h}\sum_{i=1}^{N_h} U^{m,k}_{i,l}\frac{\mathcal{X}_i(r)}{r}Y^m_l(\sigma)\right)\left(\sum_{l'=|m|}^{m_h}\sum_{i=1}^{N_h} U^{m,k'}_{j,l'}\frac{\mathcal{X}_j(r)}{r}Y^m_{l'}(\sigma)^*\right) r^2\,d\sigma\,dr$$
$$= \sum_{l=|m|}^{m_h}\sum_{i,j=1}^{N_h} U^{m,k}_{i,l}[M_0]_{ij}U^{m,k'}_{j,l} = \mathrm{Tr}\,([U^{m,k}]^T M_0 U^{m,k'}).$$

Remark 44. *An interesting observation is that, if there is no accidental degeneracy in the set of the occupied energy levels of $H^{0,\mathrm{rHF/LDA}}_{z,N}$, and if the occupied orbitals are well enough approximated in the space $\mathcal{V}^{h,m}$, then the approximate ground state density matrix $\gamma^{0,\mathrm{rHF/LDA}}_{z,N,h}$ has a unique representation of the form (4.21)-(4.23), up to the signs and the numbering of the functions $u^{h,m,k}_l$, that is up to the signs and numbering of the column vectors of the matrices $U^{m,k}$. By continuity, this uniqueness of the representation will survive if a small-enough cylindrically-symmetric perturbation is turn-on. This is the reason why this representation is well-suited to our study.*

Let us now express each component of the energy functional $\widetilde{E}^{\mathrm{rHF,LDA}}_{z,N}(\gamma_h, \beta W)$ using the representation (4.21)-(4.23) of the elements of $\mathcal{K}_{N,h}$. For this purpose, we introduce the $N_h \times N_h$ real symmetric matrices A and M_n, $n = -2, -1, 0, 1$ with entries

$$A_{ij} = \int_0^{+\infty} \mathcal{X}_i'\mathcal{X}_j' \quad \text{and} \quad [M_n]_{ij} = \int_0^{+\infty} r^n \mathcal{X}_i(r)\mathcal{X}_j(r)\,dr. \tag{4.25}$$

The weighted mass matrices M_{-2} and M_{-1} are well-defined in view of the Hardy inequality

$$\forall u \in H^1_0(0,+\infty), \quad \int_0^{+\infty}\frac{u^2(r)}{r^2}\,dr \le 4\pi\int_0^{+\infty}|u'|^2.$$

We assume from now on that the basis functions $\mathcal{X}_i$ decay fast enough at infinity for the weighted mass matrix M_1 to be well-defined.

In the representation (4.21)-(4.23), the kinetic energy is equal to

$$\frac{1}{2}\mathrm{Tr}\,(-\Delta\gamma_h) = \frac{1}{2}\sum_{\substack{-m_h\le m\le m_h\\ 1\le k\le (m_h-|m|+1)\times N_h}} n_{m,k}\left(\mathrm{Tr}\,\left([U^{m,k}]^T A U^{m,k}\right) + \mathrm{Tr}\,\left(D_m[U^{m,k}]^T M_{-2}U^{m,k}\right)\right),$$

where $D_m \in \mathbb{R}^{(m_h-|m|+1)\times(m_h-|m|+1)}$ is the diagonal matrix defined by

$$D_m = \mathrm{diag}(|m|(|m|+1), \cdots, m_h(m_h+1)). \tag{4.26}$$

All the other terms in the energy functional depending on the density

$$\rho_h := \rho_{\gamma_h} = \sum_{\substack{-m_h\le m\le m_h\\ 1\le k\le (m_h-|m|+1)N_h}} n_{m,k}|\Phi_{h,m,k}|^2, \tag{4.27}$$

we first need to express this quantity as a function of the matrices $U^{m,k}$ and the occupation numbers $n_{m,k}$. As the function ρ_h is in $\mathcal{H}^0$, we have

$$\rho_h(r,\theta) = \sum_{l=0}^{2m_h} \rho_l^h(r) Y_l^0(\theta). \tag{4.28}$$

Inserting (4.22) in (4.27), we get

$$\rho_h(r,\theta) = \sum_{\substack{-m_h \le m \le m_h \\ 1 \le k \le (m_h - |m|+1)N_h}} n_{m,k} \left| \sum_{l=|m|}^{m_h} \frac{u_l^{h,m,k}(r)}{r} Y_l^m(\theta,\varphi) \right|^2. \tag{4.29}$$

We recall the following equality [72]

$$Y_{l_1}^m (Y_{l_2}^m)^* = (-1)^m Y_{l_1}^m Y_{l_2}^{-m} = \sum_{l_3=|l_1-l_2|}^{l_1+l_2} c_{l_1,l_2,l_3}^m Y_{l_3}^0, \tag{4.30}$$

with

$$c_{l_1,l_2,l_3}^m = (-1)^m \sqrt{\frac{(2l_1+1)(2l_2+1)(2l_3+1)}{4\pi}} \begin{pmatrix} l_1 & l_2 & l_3 \\ m & -m & 0 \end{pmatrix} \begin{pmatrix} l_1 & l_2 & l_3 \\ 0 & 0 & 0 \end{pmatrix},$$

where $\begin{pmatrix} l_1 & l_2 & l_3 \\ m_1 & m_2 & m_3 \end{pmatrix}$ denote the Wigner 3j-symbols. Inserting the expansion (4.23) in (4.29) and using (4.30) and the fact that

$$\begin{pmatrix} l_1 & l_2 & l_3 \\ m_1 & m_2 & m_3 \end{pmatrix} = 0 \quad \text{unless} \quad |l_1 - l_2| \le l_3 \le l_1 + l_2,$$

we obtain

$$\rho_h(r,\theta) = \sum_{l=0}^{2m_h} \left[\sum_{i,j=1}^{N_h} \left(\sum_{\substack{-m_h \le m \le m_h \\ 1 \le k \le (m_h - |m|+1) \times N_h}} n_{m,k} \sum_{l',l''=|m|}^{m_h} c_{l',l'',l}^m U_{i,l'}^{m,k} U_{j,l''}^{m,k} \right) \frac{\mathcal{X}_i(r)}{r} \frac{\mathcal{X}_j(r)}{r} \right] Y_l^0(\theta),$$

from which we conclude that

$$\rho_l^h(r) = \sum_{i,j=1}^{N_h} \left(\sum_{\substack{-m_h \le m \le m_h \\ 1 \le k \le (m_h - |m|+1) \times N_h}} n_{m,k} \sum_{l',l''=|m|}^{m_h} c_{l',l'',l}^m U_{i,l'}^{m,k} U_{j,l''}^{m,k} \right) \frac{\mathcal{X}_i(r)}{r} \frac{\mathcal{X}_j(r)}{r}.$$

For $0 \le l \le 2m_h$, we introduce the matrix $R_l \in \mathbb{R}^{N_h \times N_h}$ defined by

$$R_l := \sum_{\substack{-m_h \le m \le m_h \\ 1 \le k \le (m_h - |m|+1) \times N_h}} n_{m,k} U^{m,k} C^{l,m} [U^{m,k}]^T \tag{4.31}$$

where $C^{l,m} \in \mathbb{R}^{(m_h-|m|+1)\times(m_h-|m|+1)}$ is the symmetric matrix[2] defined by

$$\forall |m| \leq l \leq m_h, \quad C^{l,m}_{l',l''} = \sqrt{4\pi}\, c^m_{l',l'',l}, \tag{4.32}$$

so that

$$\rho_h(r,\theta) = \frac{1}{\sqrt{4\pi}} \sum_{l=0}^{2m_h} \sum_{i,j=1}^{N_h} [R_l]_{i,j} \frac{\mathcal{X}_i(r)}{r} \frac{\mathcal{X}_j(r)}{r} Y_l^0(\theta). \tag{4.33}$$

Note that $C^{0,m}$ is the identity matrix, so that

$$R_0 = \sum_{\substack{-m_h \leq m \leq m_h \\ 1 \leq k \leq (m_h-|m|+1)\times N_h}} n_{m,k} U^{m,k} [U^{m,k}]^T$$

and

$$\mathrm{Tr}\,(M_0 R_0) = \sum_{\substack{-m_h \leq m \leq m_h \\ 1 \leq k \leq (m_h-|m|+1)\times N_h}} n_{m,k} \mathrm{Tr}\,(M_0 U^{m,k}[U^{m,k}]^T) = \sum_{\substack{-m_h \leq m \leq m_h \\ 1 \leq k \leq (m_h-|m|+1)\times N_h}} n_{m,k} = N,$$

and that $C^{1,m}$ is a symmetric tridiagonal matrix whose diagonal elements all are equal to zero.

The Coulomb attraction energy between the nucleus and the electrons then is equal to

$$\begin{aligned}
-z \int_{\mathbb{R}^3} \frac{\rho_h}{|\cdot|} &= -z \int_0^{+\infty} \int_{\mathbb{S}^2} \frac{1}{r} \left(\frac{1}{\sqrt{4\pi}} \sum_{l=0}^{2m_h} \sum_{i,j=1}^{N_h} [R_l]_{i,j} \frac{\mathcal{X}_i(r)}{r} \frac{\mathcal{X}_j(r)}{r} Y_l^0(\sigma) \right) r^2\, dr\, d\sigma \\
&= -z \int_0^{+\infty} \int_{\mathbb{S}^2} \frac{1}{r} \left(\sum_{l=0}^{2m_h} \sum_{i,j=1}^{N_h} [R_l]_{i,j} \frac{\mathcal{X}_i(r)}{r} \frac{\mathcal{X}_j(r)}{r} Y_l^0(\sigma) \right) Y_0^0(\sigma)^*\, r^2\, dr\, d\sigma \\
&= -z \sum_{i,j=1}^{N_h} [R_0]_{i,j} [M_{-1}]_{ij} = -z \mathrm{Tr}\,(M_{-1} R_0),
\end{aligned}$$

where we have used the orthonormality condition (4.15) and the fact that $Y_0^0 = \frac{1}{\sqrt{4\pi}}$.

Likewise, since $Y_1^0(\theta) = \sqrt{\frac{3}{4\pi}} \cos(\theta)$, the Stark potential (4.19) can be written in spherical coordinates as

$$W_{\mathrm{Stark}}(r,\theta) = -\sqrt{\frac{4\pi}{3}} r Y_1^0(\theta) = -\sqrt{\frac{4\pi}{3}} r Y_1^0(\theta)^*,$$

and the potential energy due to the external electric field is then equal to

$$\beta \int_{\mathbb{R}^3} \rho_h W_{\mathrm{Stark}} = -\frac{1}{\sqrt{3}} \beta \sum_{i,j=1}^{N_h} [R_1]_{ij} [M_1]_{ij} = -\frac{1}{\sqrt{3}} \beta \mathrm{Tr}\,(M_1 R_1).$$

[2]The symmetry of the matrix C^{lm} comes from the following symmetry properties of the 3j-symbols:

$$\begin{pmatrix} l_1 & l_2 & l_3 \\ m_1 & m_2 & m_3 \end{pmatrix} = (-1)^{l_1+l_2+l_3} \begin{pmatrix} l_2 & l_1 & l_3 \\ m_2 & m_1 & m_3 \end{pmatrix} = (-1)^{l_1+l_2+l_3} \begin{pmatrix} l_2 & l_1 & l_3 \\ -m_2 & -m_1 & -m_3 \end{pmatrix}.$$

Let μ be a radial, continuous function from $\mathbb{R}^3$ to $\mathbb{R}$ vanishing at infinity and such that $\int_{\mathbb{R}^3}\mu = 1$. The Coulomb interaction energy can be rewritten as follows:

$$\frac{1}{2}D(\rho_h,\rho_h) = \frac{1}{2}D\left(\rho_h - \left(\int_{\mathbb{R}^3}\rho_h\right)\mu, \rho_h - \left(\int_{\mathbb{R}^3}\rho_h\right)\mu\right) + ND(\mu,\rho_h) - \frac{N^2}{2}D(\mu,\mu). \quad (4.34)$$

The reason why we introduce the charge distribution μ is to make neutral the charge distributions $\rho_h - \left(\int_{\mathbb{R}^3}\rho_h\right)\mu$ in the first term of the right-hand side of (4.34), in such a way that the physical solution Q_{0,R_0} to the equation (4.37) below for $l = 0$ is in $H^1_0(0,+\infty)$.

Introducing the real symmetric matrix $V_\mu \in \mathbb{R}^{N_h\times N_h}$ with entries

$$[V_\mu]_{ij} = \int_0^{+\infty}[V^{\mathrm{H}}(\mu)](r\mathbf{e})\mathcal{X}_i(r)\mathcal{X}_j(r)\,dr, \quad (4.35)$$

where $\mathbf{e}$ is any unit vector of $\mathbb{R}^3$ (the value of $V^{\mathrm{H}}(\mu)(r\mathbf{e})$ is independent of $\mathbf{e}$ since $V^{\mathrm{H}}(\mu)$ is radial) the sum of the last two terms of the right-hand side of (4.34) can be rewritten as

$$ND(\mu,\rho_h) - \frac{N^2}{2}D(\mu,\mu) = N\mathrm{Tr}\left(V_\mu R_0\right) - \frac{N^2}{2}D(\mu,\mu).$$

Denoting by

$$\widetilde{V}^{\mathrm{H}}(\rho_h) = V^{\mathrm{H}}\left(\rho_h - \left(\int_{\mathbb{R}^3}\rho_h\right)\mu\right),$$

we have by symmetry $\widetilde{V}^{\mathrm{H}}(\rho_h) \in \mathcal{H}^0$ and

$$[\widetilde{V}^{\mathrm{H}}(\rho_h)](r,\theta) = \sum_{l=0}^{2m_h}\widetilde{V}_l(\rho_l^h)(r)Y_l^0(\theta) = \sum_{l=0}^{2m_h}\frac{Q_{l,R_l}(r)}{r}Y_l^0(\theta)$$

where Q_{l,R_l} is the unique solution in $H^1_0(0,+\infty)$ to the differential equation

$$-\frac{d^2Q_{l,R_l}}{dr^2}(r) + \frac{l(l+1)}{r^2}Q_{l,R_l}(r) = 4\pi r\left(\left(\frac{1}{\sqrt{4\pi}}\sum_{i,j=1}^{N_h}[R_l]_{i,j}\frac{\mathcal{X}_i(r)\mathcal{X}_j(r)}{r^2}\right) - N\mu(r)\delta_{l0}\right). \quad (4.36)$$

Note that the mappings $R_l \mapsto Q_{l,R_l}$ are linear. We therefore obtain

$$\begin{aligned}\frac{1}{2}D(\rho_h,\rho_h) =& \frac{1}{2}\sum_{l=0}^{2m_h}\frac{1}{4\pi}\left(\int_0^{+\infty}\left(\left(\frac{dQ_{l,R_l}}{dr}(r)\right)^2 + \frac{l(l+1)}{r^2}Q_{l,R_l}(r)^2\right)dr\right)\\ &+ N\mathrm{Tr}\left(V_\mu R_0\right) - \frac{N^2}{2}D(\mu,\mu). \end{aligned} \quad (4.37)$$

Finally, the exchange-correlation energy is

$$E_{\mathrm{xc}}(\rho_h) = 2\pi\int_0^{+\infty}\int_0^{\pi}\epsilon_{\mathrm{xc}}\left(\frac{1}{\sqrt{4\pi}}\sum_{l=0}^{2m_h}\sum_{i,j=1}^{N_h}[R_l]_{i,j}\frac{\mathcal{X}_i(r)}{r}\frac{\mathcal{X}_j(r)}{r}Y_l^0(\theta)\right)r^2\sin\theta\,dr\,d\theta. \quad (4.38)$$

Approximation of the Hartree term

Except for very specific basis functions (such as Gaussian atomic orbitals), it is not possible to evaluate exactly the first contribution to the Coulomb energy (4.37). It is therefore necessary to approximate it. For this purpose, we use a variational approximation of (4.36)-(4.37) in an auxiliary basis set $\{\zeta_p\}_{1\leq p\leq N_{h,\mathrm{a}}} \in (H^1_0(0,+\infty))^{N_{h,\mathrm{a}}}$, which amounts to replacing $\frac{1}{2}D(\rho_h,\rho_h)$ by its lower bound

$$\begin{aligned}\frac{1}{2}D_h(\rho_h,\rho_h) =& \frac{1}{8\pi}\left(\int_0^{+\infty}\left(\left(\frac{dQ^h_{l,R_l}}{dr}(r)\right)^2 + \frac{l(l+1)}{r^2}Q^h_{l,R_l}(r)^2\right)dr\right)\\ &+ N\mathrm{Tr}\left(V_\mu R_0\right) - \frac{N^2}{2}D(\mu,\mu),\end{aligned} \tag{4.39}$$

where Q^h_{l,R_l} is the unique solution in $\zeta^h = \mathrm{span}(\zeta_1,\cdots,\zeta_{N_{h,\mathrm{a}}})$ to the problem

$$\begin{aligned}\forall v_h \in \zeta^h, \quad &\int_0^{+\infty}\left(\frac{dQ^h_{l,R_l}}{dr}(r)\frac{dv_h}{dr}(r) + \frac{l(l+1)}{r^2}Q^h_{l,R_l}(r)v_h(r)\right)dr\\ &= 4\pi\int_0^{+\infty} r\left(\left(\frac{1}{\sqrt{4\pi}}\sum_{i,j=1}^{N_h}[R_l]_{i,j}\frac{\mathcal{X}_i(r)\mathcal{X}_j(r)}{r^2}\right) - N\mu(r)\delta_{l0}\right)v_h(r)dr,\end{aligned}$$

which is nothing but the variational approximation of (4.36) in the finite dimensional space ζ^h. Expanding the functions Q^h_{l,R_l} in the basis set $\{\zeta_k\}_{1\leq k\leq N_{h,\mathrm{a}}}$ as

$$Q^h_{l,R_l}(r) = \sum_{p=1}^{N_{h,\mathrm{a}}} Q_{p,l}\zeta_p(r),$$

and collecting the coefficients $Q_{p,l}$, $1\leq k\leq N_{h,\mathrm{a}}$ in a vector $Q_l \in \mathbb{R}^{N_{h,\mathrm{a}}}$, we obtain that the vector Q_l is solution to the linear system

$$\left(A^{\mathrm{a}} + l(l+1)M^{\mathrm{a}}_{-2}\right)Q_l = 4\pi\left(F : R_l - N\delta_{l0}G\right), \tag{4.40}$$

where the $N_{h,\mathrm{a}}\times N_{h,\mathrm{a}}$ real symmetric matrices A^{a} and M^{a}_{-2} are defined by

$$A^{\mathrm{a}}_{pq} = \int_0^{+\infty}\zeta_p'\zeta_q', \quad [M^{\mathrm{a}}_{-2}]_{pq} = \int_0^{+\infty}\frac{\zeta_p(r)\zeta_q(r)}{r^2}\,dr, \tag{4.41}$$

where $F \in \mathbb{R}^{N_{h,\mathrm{a}}\times N_h\times N_h}$ is the three-index tensor with entries

$$F_{pij} = \frac{1}{\sqrt{4\pi}}\int_0^{+\infty}\frac{\mathcal{X}_i(r)\mathcal{X}_j(r)\zeta_p(r)}{r}\,dr, \tag{4.42}$$

and where $G \in \mathbb{R}^{N_{h,\mathrm{a}}}$ is the vector with entries

$$G_p = \int_0^{+\infty} r\mu(r)\zeta_p(r)\,dr. \tag{4.43}$$

Note that since $N = \mathrm{Tr}\left(M_0R_0\right)$, the mappings $R_l \mapsto Q_l$ are in fact linear. We finally get

$$\frac{1}{2}D_h(\rho_h,\rho_h) = \frac{1}{8\pi}\sum_{l=0}^{2m_h} Q_l^T(A^{\mathrm{a}} + l(l+1)M^{\mathrm{a}}_{-2})Q_l + N\mathrm{Tr}\left(V_\mu R_0\right) - \frac{N^2}{2}D(\mu,\mu), \tag{4.44}$$

where Q_l is the solution to (4.40).

Final form of the discretized problem and Euler-Lagrange equations

We therefore end up with the following approximation of problem (4.1):

$$\widetilde{\mathcal{I}}^{\mathrm{rHF/LDA}}_{z,N,h}(\beta W) := \inf\left\{\mathcal{E}^{\mathrm{rHF/LDA}}_{z,N,\beta}((U^{m,k}),(n_{m,k})),\ (U^{m,k})_{\substack{-m_h\le m\le m_h\\ 1\le k\le (m_h-|m|+1)N_h}} \in \mathcal{U}_{N,h},\right.$$
$$\left.(n_{m,k})_{\substack{-m_h\le m\le m_h\\ 1\le k\le (m_h-|m|+1)N_h}} \in \mathcal{N}_{N,h}\right\}. \tag{4.45}$$

where

$$\begin{aligned}\mathcal{E}^{\mathrm{rHF/LDA}}_{z,N,\beta}((U^{m,k}),(n_{m,k})) :=& \frac{1}{2}\sum_{\substack{-m_h\le m\le m_h\\ 1\le k\le (m_h-|m|+1)N_h}} n_{m,k}\left(\mathrm{Tr}\,\left([U^{m,k}]^T A U^{m,k}\right) + \mathrm{Tr}\,\left(D_m[U^{m,k}]^T M_{-2}U^{m,k}\right)\right)\\ &- z\mathrm{Tr}\,(M_{-1}R_0) + \frac{1}{8\pi}\sum_{l=0}^{2m_h} Q_l^T(A^{\mathrm{a}} + l(l+1)M^{\mathrm{a}}_{-2})Q_l + N\mathrm{Tr}\,(V_\mu R_0)\\ &- \frac{N^2}{2}D(\mu,\mu) + E_{\mathrm{xc}}(\rho_h) - \frac{\beta}{\sqrt{3}}\mathrm{Tr}\,(M_1R_1),\end{aligned}$$

where for each l, the matrix R_l and the vector Q_l are respectively defined by (4.31) and (4.40), and where the last but one term in the right-hand side is given by (4.38).

The gradient of $\widetilde{\mathcal{I}}^{\mathrm{rHF/LDA}}_{z,N,h}(\beta W)$ with respect to $U^{m,k}$ is

$$\begin{aligned}\nabla_{U^{m,k}}\mathcal{E}^{\mathrm{rHF/LDA}}_{z,N,\beta} =& 2n_{m,k}\left(\frac{1}{2}AU^{m,k} + \frac{1}{2}M_{-2}U^{m,k}D_m - zM_{-1}U^{m,k} + NV_\mu U^{m,k}\right.\\ &\left. + \sum_{l=0}^{2m_h}(Q_l^T\cdot F)(U^{m,k}C^{l,m}) + \sum_{l=0}^{2m_h} V^l_{\mathrm{xc}}U^{m,k}C^{l,m} - \frac{\beta}{\sqrt{3}}M_1U^{m,k}C^{1,m}\right),\end{aligned}$$

where for each $0\le l\le 2m_h$, the $N_h\times N_h$ real matrix V^l_{xc} is defined by

$$[V^l_{\mathrm{xc}}]_{ij} = \sqrt{\pi}\int_0^{+\infty}\int_0^{\pi} v_{\mathrm{xc}}\left(\frac{1}{\sqrt{4\pi}}\sum_{i,j=1}^{N_h}[R_l]_{i,j}\frac{\mathcal{X}_i(r)\mathcal{X}_j(r)}{r^2}\right)\mathcal{X}_i(r)\mathcal{X}_j(r)Y_l^0(\theta)\,\sin\theta\,dr\,d\theta, \tag{4.46}$$

where $v_{\mathrm{xc}}(\rho) := \frac{de_{\mathrm{xc}}}{d\rho}(\rho)$ is the exchange-correlation potential.

Diagonalizing simultaneously the Kohn-Sham Hamiltonian and the ground state density matrix in an orthonormal basis, we obtain that the ground state can be obtained by solving the following system of first-order optimality conditions, which is nothing but a reformulation of the discretized extended Kohn-Sham equations exploiting the cylindrical

symmetry of the problem:

$$\frac{1}{2}AU^{m,k} + \frac{1}{2}M_{-2}U^{m,k}D_m - zM_{-1}U^{m,k} + NV_\mu U^{m,k} + \sum_{l=0}^{2m_h}(Q_l^T \cdot F)(U^{m,k}C^{l,m}) + \sum_{l=0}^{2m_h} V_{\rm xc}^l U^{m,k}C^{l,m} - \frac{1}{\sqrt{3}}\beta M_1 U^{m,k}C^{1,m} = \epsilon_{m,k}M_0U^{m,k}, \tag{4.47}$$

$$\mathrm{Tr}\left([U^{m,k}]^T M_0 U^{m,k'}\right) = \delta_{kk'}, \tag{4.48}$$

$$\left(A^{\rm a} + l(l+1)M_{-2}^{\rm a}\right)Q_l = F : R_l - \mathrm{Tr}\,(M_0R_0)\delta_{l0}G, \tag{4.49}$$

$$[V_{\rm xc}^l]_{ij} = \sqrt{\pi}\int_0^{+\infty}\int_0^{\pi} v_{\rm xc}\left(\frac{1}{\sqrt{4\pi}}\sum_{i,j=1}^{N_h}[R_l]_{i,j}\frac{\mathcal{X}_i(r)\mathcal{X}_j(r)}{r^2}\right)\mathcal{X}_i(r)\mathcal{X}_j(r)Y_l^0(\theta)\,\sin\theta\,dr\,d\theta, \tag{4.50}$$

$$n_{m,k} = 2 \text{ if } \epsilon_{m,k} < \epsilon_{\rm F}, \quad 0 \le n_{m,k} \le 2 \text{ if } \epsilon_{m,k} = \epsilon_{\rm F}, \quad n_{m,k} = 0 \text{ if } \epsilon_{m,k} > \epsilon_{\rm F}, \tag{4.51}$$

$$\sum_{\substack{-m_h\le m\le m_h\\ 1\le k\le (m_h-|m|+1)N_h}} n_{m,k} = N, \tag{4.52}$$

$$R_l = \sum_{\substack{-m_h\le m\le m_h\\ 1\le k\le (m_h-|m|+1)N_h}} n_{m,k}U^{m,k}C^{l,m}[U^{m,k}]^T, \tag{4.53}$$

where the matrices A, M_{-2}, M_{-1}, M_0, M_1, D_m, V_μ, $A^{\rm a}$, $M_{-2}^{\rm a}$, $C^{l,m}$, the 3-index tensor F and the vector G are defined by (4.25), (4.26), (4.32), (4.41), (4.42), (4.43).

$\mathbb{P}_4$-finite element method

In our calculations, we use the same approximation space to discretize the radial components of the Kohn-Sham orbitals and the radial Poisson equations (4.36), so that, in our implementation of the method, $N_{h,\rm a} = N_h$ and $\mathcal{X}^h = \zeta^h$. We choose a cut-off radius $L_e > 0$ large enough and discretize the interval $[0, L_e]$ using a non-uniform grid with $N_I + 1$ points $0 = r_1 < r_2 < \cdots < r_{N_I} < r_{N_I+1} = L_e$. The positions of the points are chosen according to the following rule:

$$r_k = r_{k-1} + h_k, \qquad h_{N_I} = \frac{1-s}{1-s^{N_I}}L_e, \qquad h_{k-1} = sh_k,$$

where $0 < s < 1$ is a scaling parameter leading to a progressive refinement of the mesh when one gets closer to the nucleus ($r = 0$). To achieve the desired accuracy, we use the $\mathbb{P}_4$-finite element method.

All the terms in the variational discretization of the energy and of the constraints can be computed exactly (up to finite arithmetics errors), except the exchange-correlation terms (4.38) and (4.46), which requires a numerical quadrature method. In our calculation, we use Gauss quadrature formulas of the form

$$\int_0^{+\infty}\int_0^{\pi} f(r,\theta)\sin\theta\,dr\,d\theta = \int_0^{+\infty}\int_{-1}^{1} f(r,\arccos t_\theta)\,dr\,dt_\theta$$
$$\simeq \sum_{k=1}^{N_I}\sum_{i=1}^{N_{\mathrm{g},r}}\sum_{j=1}^{N_{\mathrm{g},\theta}} h_k w_{i,\mathrm{r}} w_{j,\theta} f(r_k + h_k t_{i,\mathrm{r}}, \arccos(t_{j,\theta})),$$

where the $0 < t_{1,r} < \cdots < t_{N_{\mathrm{g},r},r} < 1$ (resp. $-1 < t_{1,\theta} < \cdots < t_{N_{\mathrm{g},\theta},\theta} < 1$) are Gauss points for the r-variable (resp. for the t_θ-variable) with associated weights $w_{1,r},\cdots,w_{N_{\mathrm{g},r},r}$ (resp. $w_{1,\theta},\cdots,w_{N_{\mathrm{g},\theta},\theta}$).

More details about the practical implementation of the method are provided in Appendix.

4.3.2 Description of the algorithm

In order to solve the self-consistent equations (4.47), we use an iterative algorithm. For clarity, we first present this algorithm within the continuous setting. Its formulation in the discretized setting considered here is detailed below. The iterations are defined as follows: an Ansatz of the ground state density $\rho^{[n]}$ being known,

1. construct the Kohn-Sham operator

$$H^{[n]} = -\frac{1}{2}\Delta - \frac{z}{|\cdot|} + V^{\mathrm{H}}(\rho^{[n]}) + v_{\mathrm{xc}}(\rho^{[n]}) + \beta W$$

   where $v_{\mathrm{xc}} = 0$ for the rHF model and $v_{\mathrm{xc}} = v_{\mathrm{xc}}^{\mathrm{LDA}}$ for the Kohn-Sham LDA model;

2. for each $m \in \mathbb{Z}$, compute the negative eigenvalues of $H_m^{[n]} := \Pi_m H^{[n]} \Pi_m$, where Π_m is the orthogonal projector on the space $\mathcal{H}^m$:

$$H_m^{[n]}\phi_{m,k}^{[n+1]} = \epsilon_{m,k}^{[n+1]}\phi_{m,k}^{[n+1]}, \qquad \int_{\mathbb{R}^3} \phi_{m,k}^{[n+1]*}\phi_{m,k'}^{[n+1]} = \delta_{kk'};$$

3. construct a new density

$$\rho_*^{[n+1]} = \sum_{m,k} n_{m,k}^{[n+1]} |\phi_{m,k}^{[n+1]}|^2,$$

   where

$$\begin{cases} n_{m,k}^{[n+1]} = 2 & \text{if} \quad \epsilon_{m,k}^{[n+1]} < \epsilon_{\mathrm{F}}^{[n+1]}, \\ 0 \le n_{m,k}^{[n+1]} \le 2 & \text{if} \quad \epsilon_{m,k}^{[n+1]} = \epsilon_{\mathrm{F}}^{[n+1]}, \\ n_{m,k}^{[n+1]} = 0 & \text{if} \quad \epsilon_{m,k}^{[n+1]} > \epsilon_{\mathrm{F}}^{[n+1]}, \end{cases} \qquad \text{and} \qquad \sum_{(m,k)} n_{m,k}^{[n+1]} = N;$$

4. update the density:
$$\rho^{[n+1]} = t_n \rho_*^{[n+1]} + (1 - t_n)\rho^{[n]},$$
where $t_n \in [0, 1]$ either is a fixed parameter independent of n and chosen *a priori*, or is optimized using the Optimal Damping Algorithm (ODA), see below;

5. if some convergence criterion is satisfied, then stop; else, replace n with $n+1$ and go to step 1.

In the non-degenerate case, that is when $\epsilon_{\mathrm{F}}^{[n+1]}$ is not an eigenvalue of the Hamiltonian $H^{[n]}$, the occupation numbers $n_{m,k}^{[n+1]}$ are equal to either 0 (unoccupied) or 2 (fully occupied), while in the degenerate case the occupation numbers at the Fermi level have to be determined. We distinguish two cases: if $W = 0$, or more generally if W is spherically symmetric, and if $\epsilon_{\mathrm{F}}^{[n+1]}$ is not an accidentally degenerate eigenvalue of $H^{[n]}$, then the occupation numbers at the Fermi level are all equal; otherwise, the occupations numbers are not known *a priori*. In our approach we select the occupation numbers at the Fermi level which provide the lowest Kohn-Sham energy. When the degenerate eigenspace at the Fermi level is of dimension 3, that is when the highest energy partially occupied orbitals are perturbations of a three-fold degenerate p-orbital, the optimal occupation numbers can be found by using the bisection method since, in this case, the search space can be parametrized by a single real-valued parameter (this is due to the fact that the sum of the three occupation numbers is fixed and that two of them are equal by cylindrically symmetric). In the general case, more generic optimization methods have to be resorted to.

In the discretization framework we have chosen, the algorithm can be formulated as follows.

Initialization.

1. Choose the numerical parameters m_h (cut-off in the spherical harmonics expansion), L_e (size of the simulation domain for the radial components of the Kohn-Sham orbitals and the electrostatic potential), N_I (size of the mesh for solving the radial equations), $N_{\mathrm{g},r}$ (number of Gauss points for the radial quadrature formula), $N_{\mathrm{g},\theta}$ (number of Gauss points for the angular quadrature formula), and $\varepsilon > 0$ (convergence threshold),

2. assemble the matrices $A = A^{\mathrm{a}}$, $M_{-2} = M_{-2}^{\mathrm{a}}$, M_{-1}, M_0, M_1, C^{lm}, V_μ and the vector G. The tensor F can be either computed once and for all, or the contractions $F : R_l^{[n]}$ can be computed on the fly, depending on the size of the discretization parameters and the computational means available;

3. choose an initial guess $(R_l^{[0]})_{0 \le l \le 2m_h}$ for the matrices representing the discretized ground state density at iteration 0 (it is possible to take $R_l = 0$ for all l if no other better guess is known).

Iterations. The matrices $(R_l^{[n]})_{0 \le l \le 2m_h}$ at iteration n being known,

1. construct the building blocks of the discretized analogues of the operators $H_m^{[n]}$. For this purpose,

(a) solve, for each $l = 0, \cdots, 2m_h$, the linear equation

$$\left(A^{\mathrm{a}} + l(l+1)M^{\mathrm{a}}_{-2}\right) Q_l^{[n]} = 4\pi \left(F : R_l^{[n]} - N\delta_{l0}G\right)$$

(b) assemble, for each $l = 0, \cdots, 2m_h$, the matrix $V_l^{\mathrm{xc},[n]}$ by means of use Gauss quadrature rules

$$[V_{\mathrm{xc}}^{l,[n]}]_{ij} = \sqrt{\pi} \sum_{k=1}^{N_I} \sum_{p=1}^{N_{\mathrm{g},r}} \sum_{q=1}^{N_{\mathrm{g},\theta}} h_k w_{p,\mathrm{r}} w_{q,\theta} f_{ij}^l(r_k + h_k t_{p,\mathrm{r}}, t_{q,\theta}),$$

where

$$f_{ij}^l(r, t_\theta) = v_{\mathrm{xc}} \left(\frac{1}{\sqrt{4\pi}} \sum_{l=0}^{m_h} \sum_{i,j=1}^{N_h} [R_l]_{i,j} \frac{\mathcal{X}_i(r)\mathcal{X}_j(r)}{r^2} Y_l^0(\arccos t_\theta) \right) \mathcal{X}_i(r)\mathcal{X}_j(r) Y_l^0(\arccos t_\theta);$$

2. solve, for each $-m_h \leq m \leq m_h$, the generalized eigenvalue problem

$$\frac{1}{2}AU^{m,k,[n+1]} + \frac{1}{2}M_{-2}U^{m,k,[n+1]}D_m - zM_{-1}U^{m,k,[n+1]} + NV_\mu U^{m,k,[n+1]} + \sum_{l=0}^{2m_h} (Q_l^{[n]T} \cdot F)(U^{m,k,[n+1]}C^{l,m}) + \sum_{l=0}^{2m_h} V_{\mathrm{xc}}^{l,[n]} U^{m,k,[n+1]} C^{l,m} - \frac{\beta}{\sqrt{3}} M_1 U^{m,k,[n+1]} C^{1,m} = \epsilon_{m,k}^{[n+1]} M_0 U^{m,k,[n+1]}, \tag{4.54}$$

$$\mathrm{Tr}\left([U^{m,k,[n+1]}]^T M_0 U^{m,k',[n+1]} \right) = \delta_{kk'}, \tag{4.55}$$

3. build the matrices $R_{l,*}^{[n+1]}$ using the *Aufbau* principle and, if necessary, optimizing the occupation numbers $n_{m,k}^{[n+1]}$, by selecting the occupation numbers at the Fermi level leading to the lowest Kohn-Sham energy[3]:

$$R_{l,*}^{[n+1]} = \sum_{\substack{-m_h \leq m \leq m_h \\ 1 \leq k \leq (m_h - |m| + 1)N_h}} n_{m,k}^{[n+1]} U^{m,k,[n+1]} C^{l,m} [U^{m,k,[n+1]}]^T,$$

where

$$\begin{cases} n_{m,k}^{[n+1]} = 2 & \text{if} \quad \epsilon_{m,k}^{[n+1]} < \epsilon_{\mathrm{F}}^{[n+1]}, \\ 0 \leq n_{m,k}^{[n+1]} \leq 2 & \text{if} \quad \epsilon_{m,k}^{[n+1]} = \epsilon_{\mathrm{F}}^{[n+1]}, \\ n_{m,k}^{[n+1]} = 0 & \text{if} \quad \epsilon_{m,k}^{[n+1]} > \epsilon_{\mathrm{F}}^{[n+1]}, \end{cases} \qquad \text{and} \qquad \sum_{(m,k)} n_{m,k}^{[n+1]} = N;$$

[3] In practice, this optimization problem is low-dimensional. Indeed, the degeneracy of the Fermi level is typically 3 (perturbation of p-orbitals) or 5 (perturbation of d-orbitals) for most atoms of the first four rows of the periodic table, and some of the occupation numbers are known to be equal for symmetric reasons.

4. update the density:

$$\forall 0 \leq l \leq 2m_h, \quad R_l^{[n+1]} = t_n R_{l,*}^{[n+1]} + (1-t_n) R_l^{[n]},$$

where $t_n \in [0,1]$ either is a fixed parameter independent of n and chosen *a priori*, or is optimized using the ODA, see below;

5. if (for instance) $\max_{0\leq l\leq 2m_h} \|R_l^{[n+1]} - R_l^{[n]}\| \leq \varepsilon$ then stop; else go to step one.

Note that the generalized eigenvalue problem (4.54)-(4.55) can be rewritten as a standard generalized eigenvalue problem of the form

$$\mathbb{H}^m \mathbb{V}_k = \epsilon_{m,k}^{[n+1]} \mathbb{M} \mathbb{V}_k, \qquad \mathbb{V}_k^T \mathbb{M} \mathbb{V}_{k'} = \delta_{kk'}, \tag{4.56}$$

where the unknowns are vectors (and not matrices) by introducing the column vectors $\mathbb{V}_k \in \mathbb{R}^{(m_h+1-|m|)N_h}$ and the block matrices

$$\mathbb{H}^m \in \mathbb{R}^{(m_h+1-|m|)N_h \times (m_h+1-|m|)N_h} \qquad \text{and} \qquad \mathbb{M} \in \mathbb{R}^{(m_h+1-|m|)N_h \times (m_h+1-|m|)N_h}$$

defined as

$$\mathbb{V}_k = \begin{pmatrix} U_{\cdot,|m|}^{m,k,[n+1]} \\ \hline \cdot \\ \cdot \\ \cdot \\ \hline U_{\cdot,m_h}^{m,k,[n+1]} \end{pmatrix}, \qquad \mathbb{H}^m = \left(\begin{array}{c|c|c|c|c} \mathbb{H}^m_{|m|,|m|} & \mathbb{H}^m_{|m|,|m|+1} & \cdots & \mathbb{H}^m_{|m|,m_h-1,} & \mathbb{H}^m_{|m|,m_h} \\ \hline \mathbb{H}^m_{|m|+1,|m|} & \mathbb{H}^m_{|m|+1,|m|+1} & \cdots & \mathbb{H}^m_{|m|+1,m_h-1,} & \mathbb{H}^m_{|m|+1,m_h} \\ \hline \cdots & \cdots & \cdots & \cdots & \cdots \\ \hline \mathbb{H}^m_{m_h-1,|m|} & \mathbb{H}^m_{m_h-1,|m|+1} & \cdots & \mathbb{H}^m_{m_h-1,m_h-1,} & \mathbb{H}^m_{m_h-1,m_h} \\ \hline \mathbb{H}^m_{m_h,|m|} & \mathbb{H}^m_{m_h,|m|+1} & \cdots & \mathbb{H}^m_{m_h,m_h-1,} & \mathbb{H}^m_{m_h,m_h} \end{array}\right),$$

and

$$\mathbb{M} = \text{block diag}(M_0, \cdots, M_0),$$

where each of the $(m_h - |m| + 1)$ block $\mathbb{H}^m_{l,l'}$ is of size $N_h \times N_h$ with

$$\forall |m| \leq l \leq m_h, \quad \mathbb{H}^m_{l,l} = \frac{1}{2}A + \frac{l(l+1)}{2} M_{-2} - zM_{-1} + NV_\mu + \sum_{l''=0}^{2m_h} C^{l,m}_{l,l''} \left([Q^{[n]}_{l''}]^T \cdot F + V_{\text{xc}}^{l'',[n]} \right)$$

$$\forall |m| \leq l \neq l' \leq m_h, \quad \mathbb{H}^m_{l,l'} = \sum_{l''=0}^{2m_h} C^{l,m}_{l',l''} \left([Q^{[n]}_{l''}]^T \cdot F + V_{\text{xc}}^{l'',[n]} \right) - \frac{\beta}{\sqrt{3}} C^{1,m} M_1 \delta_{|l-l'|,1}.$$

If $\beta = 0$ and if the density $\rho_h^{[n]}$ is radial, then $R_l^{[n]} = 0$ for all $l \in \mathbb{N}^*$, and the matrix $\mathbb{H}^m$ is block diagonal. The generalized eigenvalue problem (4.56) can then be decoupled in $(m_h - |m| + 1)$ independent generalized eigenvalue problems of size N_h. This comes from the fact that the problem being spherically symmetric, the Kohn-Sham Hamiltonian is block diagonal in the two decompositions

$$L^2(\mathbb{R}^3) = \bigoplus_{l\in\mathbb{N}} \mathcal{H}_l \qquad \text{and} \qquad L^2(\mathbb{R}^3) = \bigoplus_{m\in\mathbb{Z}} \mathcal{H}^m.$$

Let us conclude this section with some remarks on the Optimal Damping Algorithm (ODA) [20, 19], used to find an optimal step-length t_n to mix the matrices $R_{l,*}^{[n+1]}$ and $R_l^{[n]}$

in Step 4 of the iterative algorithm. This step-length is obtained by minimizing on the range $t \in [0,1]$ the one-dimensional function

$$t \mapsto \widetilde{E}^{\mathrm{rHF/LDA}}_{z,N}\left((1-t)\gamma^{[n+1]}_* + t\gamma^{[n]}, \beta W\right),$$

where $\gamma^{[n]}$ is the current approximation of the ground state density matrix at iteration n and

$$\gamma^{[n+1]}_* = \sum_{\substack{-m_h \le m \le m_h \\ 1 \le k \le (m_h - |m|+1)N_h}} n^{[n+1]}_{m,k} |\Phi^{[n+1]}_{h,m,k}\rangle\langle\Phi^{[n+1]}_{h,m,k}|,$$

with

$$\Phi^{[n+1]}_{h,m,k}(r,\theta,\varphi) = \sum_{l=|m|}^{m_h} \sum_{i=1}^{N_h} U^{m,k,[n+1]}_{i,l} \frac{\mathcal{X}_i(r)}{r} Y^m_l(\theta,\varphi),$$

A key observation is that this optimization problem can be solved without storing density matrices, but only the two sets of matrices $R^{[n]} := (R^{[n]}_l)_{0 \le l \le 2m_h}$ and $R^{[n+1]}_* := (R^{[n+1]}_{l,*})_{0 \le l \le 2m_h}$, and the scalars

$$E^{[n]}_{\mathrm{kin}} := \mathrm{Tr}\left(-\frac{1}{2}\Delta\gamma^{[n]}\right)$$

and

$$\begin{aligned} E^{[n+1]}_{\mathrm{kin},*} &:= \mathrm{Tr}\left(-\frac{1}{2}\Delta\gamma^{[n+1]}_*\right) \\ &= \frac{1}{2} \sum_{\substack{-m_h \le m \le m_h \\ 1 \le k \le (m_h - |m|+1)\times N_h}} n^{[n+1]}_{m,k} \Big(\mathrm{Tr}\left([U^{m,k,[n+1]}]^T A U^{m,k,[n+1]}\right) \\ &\qquad + \mathrm{Tr}\left(D_m [U^{m,k,[n+1]}]^T M_{-2} U^{m,k,[n+1]}\right)\Big), \end{aligned}$$

Indeed, we have for all $t \in [0,1]$,

$$\widetilde{E}^{\mathrm{rHF/LDA}}_{z,N}\left((1-t)\gamma^{[n+1]}_* + t\gamma^{[n]}, \beta W\right) = (1-t)E^{[n+1]}_{\mathrm{kin},*} + tE^{[n]}_{\mathrm{kin}} + \mathcal{F}^{\mathrm{rHF/LDA}}\left((1-t)R^{[n+1]}_* + tR^{[n]}, \beta W\right),$$

where the functional $\mathcal{F}^{\mathrm{rHF/LDA}}$ collects all the terms of the Kohn-Sham functional depending on the density only. When $E_{\mathrm{xc}} = 0$ (rHF model), the function

$$t \mapsto \widetilde{E}^{\mathrm{rHF/LDA}}_{z,N}\left((1-t)\gamma^{[n+1]}_* + t\gamma^{[n]}, \beta W\right)$$

is a convex polynomial of degree two, and its minimizer on $[0,1]$ can therefore be easily computed explicitly. In the LDA case, the minimum on $[0,1]$ of the above function of t can be obtained using any line search method. We use here the golden search method [66, Chapter 10]. Once the minimizer t_n is found, the quantity $E^{[n]}_{\mathrm{kin}}$ is updated using the relation

$$E^{[n+1]}_{\mathrm{kin}} = (1-t_n)E^{[n+1]}_{\mathrm{kin},*} + t_n E^n_{\mathrm{kin}}.$$

4.4 Numerical results

As previously mentioned, we use in our code the same basis to discretize the radial components of the Kohn-Sham orbitals and of the Hartree potential, that is $(\mathcal{X}_i)_{1\leq i\leq N_h} = (\zeta_i)_{1\leq i\leq N_h}$, and the $\mathbb{P}_4$ finite elements method to construct the discretization basis.

We start this section by studying the convergence rate of the ground state energy and of the occupied energy levels of the carbon atom ($z = 6$) as functions of the cut-off radius L_e and the mesh size N_I (see Section 4.3.1). The errors on the total energy and on the occupied energy levels for the rHF model are plotted in Fig. 4.1 (for $L_e = 50$ and different values of N_I) and Fig. 4.2 (for $N_I = 50$ and different values of L_e), the reference calculation corresponding to $L_e = 100$ and $N_I = 100$. We can see that the choice $L_e = 50$ and $N_I = 50$ provide accuracies of about 1 μHa (recall that chemical accuracy corresponds to 1 mHa). Similar results are obtained for the Xα model.

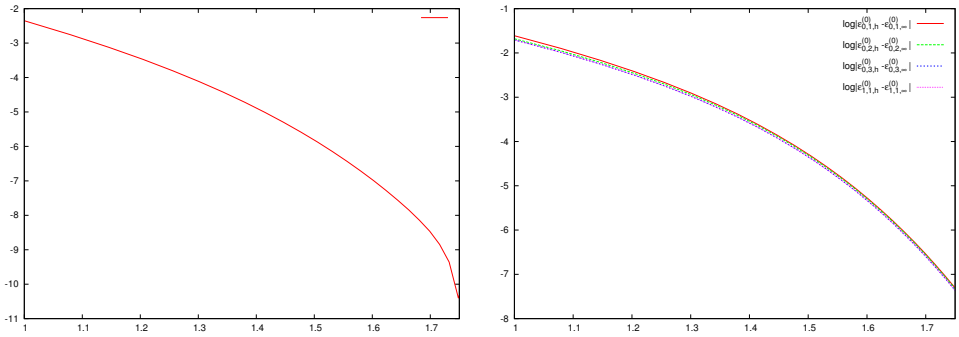


Figure 4.1 – Error on the total energy (left) and the occupied energy level (right) of the carbon atom for the rHF model as a function of the cut-off radius L_e for a fixed mesh size $N_I = 50$ (the reference calculation corresponds to $L_e = 100$ and $N_I = 100$).

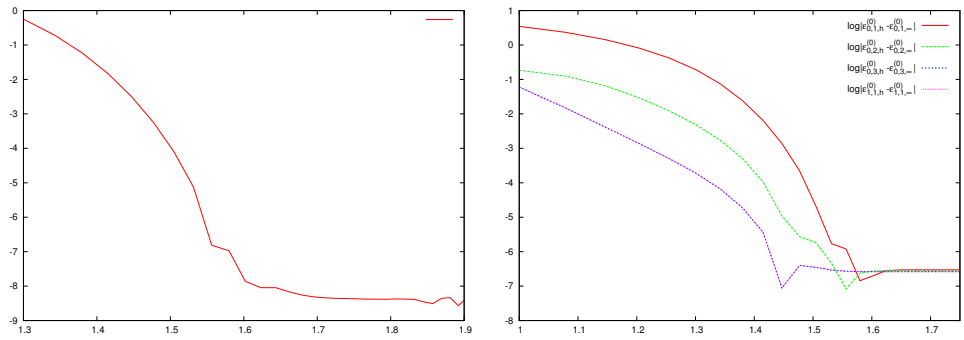


Figure 4.2 – Error on the total energy (left) and the occupied energy level (right) of the carbon atom for the rHF model as a function of the mesh size N_I, for a fixed cut-off radius $L_e = 50$ (the reference calculation corresponds to $L_e = 100$ and $N_I = 100$).

4.4.1 Electronic structures of isolated atoms

We report here calculations on all the atoms of the first four rows of the periodic table obtained with the rHF (Section 4.4.1) and Xα (Section 4.4.1) models respectively.

Occupied energy levels in the rHF model

The negative eigenvalues of $H_{\rho^0}^{\mathrm{rHF}}$ for all $1 \leq z \leq 54$ (first four rows of the periodic table) are listed in the tables below. The results for $1 \leq z \leq 20$, $27 \leq z \leq 39$, $42 \leq z \leq 45$ and $48 \leq z \leq 54$ correspond to $L_e = 50$ and $N_I = 50$ (these values are sufficient to obtain chemical accuracy). The remaining atoms are more difficult to deal with because the Fermi level happens to be an accidentally degenerate eigenvalue associated with

- the 4p and 3d shells for $z = 21$ and $z = 22$;
- the 5s and 3d shells for $23 \leq z \leq 26$, with a Fermi level very close (or possibly equal) to zero;
- the 5p and 4d shells for $z = 40$, with a Fermi level very close (or possibly equal) to zero;
- the 6s and 4d shells for $z = 41$ and $z = 42$, with a Fermi level very close (or possibly equal) to zero;
- the 5s and 4d shells for $z = 46$ and $z = 47$.

Since the radial component of the highest occupied orbital typically vanishes as $e^{-\sqrt{2|\epsilon_{z,z,\mathrm{F}}^{0,\mathrm{rHF}}|}r}$ if $\epsilon_{z,NF}^{0,\mathrm{rHF}} < 0$ and algebraically if $\epsilon_{z,z,\mathrm{F}}^{0,\mathrm{rHF}} = 0$, we used $L_e = 200$ and $N_I = 100$ for the atoms for which the Fermi level is very close or possibly equal to zero. In the next version of the code, we will implement Robin boundary conditions to deal with these cases. When the accidental degeneracy involves an s-shell and since the density is radial, the problem of finding the occupation numbers at the Fermi level reduces to finding a single parameter $t_0 \in [0, 1]$, which encodes the amount of electrons on the upper s-shell. In other word, one can write

$$\rho_{z,z}^{0,\mathrm{rHF}} = \rho_f + t_0\rho_{\mathrm{s}} + (1 - t_0)\rho_{\mathrm{d}},$$

where ρ_f is the density corresponding to the fully occupied shells, and where ρ_{s} and ρ_{d} are densities corresponding to the accidentally degenerate s and d shells. Using the same trick for accidentally degenerate p and d shells, we manage to obtain a self-consistent solution to the rHF equations, which is necessarily a ground state since the rHF model in convex in the density matrix.

Hydrogen and Helium:

z	1s
1	-0.046222441
2	-0.18488978

First row:

z	1s	2s	2p
3	-1.20270301	-0.01322136	-
4	-2.90243732	-0.04372294	-
5	-5.40709672	-0.16484895	-0.00228929
6	-8.55573207	-0.26568197	-0.01204656
7	-12.39017752	-0.38469911	-0.02731211
8	-16.91253830	-0.52288300	-0.04728083
9	-22.12352496	-0.68047933	-0.07166353
10	-28.02348145	-0.85759726	-0.10342071

Second row:

z	1s	2s	2p	3s	3p
11	-35.06531327	-1.45387137	-0.51433947	-0.01247334	-
12	-42.96317835	-2.16934853	-1.03789169	-0.03403618	-
13	-51.83361292	-3.11883641	-1.78980637	-0.13539872	-0.00236049
14	-61.53217897	-4.16012798	-2.62905505	-0.20880306	-0.01076743
15	-72.08395183	-5.31952891	-3.58242198	-0.28419984	-0.02343144
16	-83.48974606	-6.59848973	-4.65155127	-0.36358542	-0.03974632
17	-95.74953576	-7.99740416	-5.83693061	-0.44762885	-0.05940137
18	-108.86319120	-9.51643491	-7.13877263	-0.53666989	-0.08223377

Third row:

z	1s	2s	2p	3s	3p	4s
19	-123.09371155	-11.41336398	-8.81578407	-0.86617519	-0.32610851	-0.00949680
20	-138.23385507	-13.47856459	-10.65883777	-1.22593632	-0.59655446	-0.02427523

z	1s	2s	2p	3s	3p	4s	4p	3d	t_0 on 3d
21	-154.3586	-15.7853	-12.7415	-1.6900	-0.9696	-0.0864	-0.0026	-0.0026	0.028
22	-171.131	-17.9548	-14.6900	-1.9168	-1.1152	-0.0082	-0.0005	-0.0005	1.5380

z	1s	2s	2p	3s	3p	4s	5s	3d	t_0 on 5s
23	-188.7708	-20.2407	-16.7539	-2.15109	-1.26708	-0.07796	-0.00044	-0.00044	0.1689
24	-207.2745	-22.6427	-18.9327	-2.3922	-1.4240	-0.0702	-0.00020	-0.00020	0.1028
25	-226.6420	-25.1593	-21.2249	-2.6388	-1.5844	-0.0638	-0.00005	-0.00005	0.0566
26	-246.8743	-27.7923	-23.6325	-2.8922	-1.7496	-0.0582	0.00006	0.00006	0.0214

z	1s	2s	2p	3s	3p	4s	3d
27	-267.97358	-30.54466	-26.15796	-3.15500	-1.92170	-0.05437	-0.00119
28	-289.94359	-33.42047	-28.80557	-3.43107	-2.10456	-0.05459	-0.00722
29	-312.78011	-36.41574	-31.57124	-3.71624	-2.29392	-0.05539	-0.01370
30	-336.48291	-39.53046	-34.45490	-4.01038	-2.48957	-0.05646	-0.02026

z	1s	2s	2p	3s	3p	3d	4s	4p
31	-361.30915373	-43.03685995	-37.72686012	-4.57587907	-2.95111519	-0.26410850	-0.16513180	-0.00225054
32	-387.03964375	-46.71169384	-41.16430511	-5.18276103	-3.44948249	-0.53374871	-0.22933666	-0.01054116
33	-413.70410266	-50.58386786	-44.79632026	-5.85675241	-4.01109639	-0.86072524	-0.29329191	-0.02257476
34	-441.29732764	-54.64718844	-48.61688712	-6.59013132	-4.62885611	-1.24022451	-0.35879526	-0.03741385
35	-469.81532351	-58.89678392	-52.62128841	-7.37731085	-5.29767763	-1.66831339	-0.42619337	-0.05462542
36	-499.25546693	-63.32932357	-56.80632165	-8.21464148	-6.01429770	-2.14232300	-0.49563869	-0.07399144

Fourth row:

z	1s	2s	2p	3s	3p	3d	4s	4p	5s	5p
37	-529.82601790	-68.15068857	-61.37833545	-9.30643156	-6.98331877	-2.86700686	-0.76009595	-0.27190798	-0.00873608	-
38	-561.33920001	-73.17198115	-66.14866074	-10.46284560	-8.01515628	-3.65305106	-1.03266673	-0.47589319	-0.02158602	-
39	-593.86428446	-78.46184644	-71.18601398	-11.75196775	-9.17808919	-4.56895864	-1.38316482	-0.75715385	-0.07643896	-0.00257626

z	1s	2s	2p	3s	3p	3d	4s	4p	5s	5p	4d	t_0 on 4d
40	-627.1736	-83.7796	-76.2511	-12.9368	-10.2352	-5.3771	-1.5820	-0.8924	-0.0736	-0.0004	-0.0004	1.603

z	1s	2s	2p	3s	3p	3d	4s	4p	5s	6s	4d	t_0 on 6s
41	-661.3853	-89.2541	-81.4718	-14.1458	-11.3153	-6.2066	-1.7642	-1.0128	-0.0626	-0.0001	-0.0001	0.0079
42	-696.5125	-94.8971	-86.8598	-15.3909	-12.4302	-7.0694	-1.9422	-1.1300	-0.0494	0.0001	0.0001	0.0076

z	1s	2s	2p	3s	3p	3d	4s	4p	5s	4d
43	-732.56043462	-100.7181380	-92.42481893	-16.68177062	-13.58963868	-7.97538494	-2.12654690	-1.25415793	-0.04455432	-0.00944404
44	-769.53351308	-106.7135989	-98.16322266	-18.01497015	-14.79032927	-8.92098014	-2.31409507	-1.38184648	-0.04320371	-0.02418577
45	-807.42521	-112.88068	-104.07219	-19.38777	-16.02955	-9.90351	-2.50245	-1.51046	-0.04269	-0.04081

z	1s	2s	2p	3s	3p	3d	4s	4p	5s	4d	t_0 on 5s
46	-846.2173	-119.1903	-110.1229	-20.7717	-17.2789	-10.8943	-2.6643	-1.6133	-0.0384	-0.0384	1.6723
47	-885.906	-125.669	-116.341	-22.192	-18.564	-11.919	-2.824	-1.714	-0.033	-0.033	1.353

z	1s	2s	2p	3s	3p	3d	4s	4p	4d	5s	5p
48	-926.60969514	-132.40974761	-122.82066065	-23.74286025	-19.97783049	-13.07178064	-3.07367236	-1.90166791	-0.09671315	-0.04286172	-
49	-968.39851855	-139.49293764	-129.64090781	-25.50170538	-21.59919010	-14.43055667	-3.48770732	-2.25177074	-0.31074362	-0.13152493	-0.00244819
50	-1011.10988776	-146.75529247	-136.63892941	-27.30519988	-23.26432592	-15.83203278	-3.90095895	-2.59906146	-0.51756218	-0.18185504	-0.010597961
51	-1054.77491808	-154.22790173	-143.84587070	-29.18404362	-25.00398086	-17.30702665	-4.34350846	-2.97392511	-0.74975726	-0.23082157	-0.021622274
52	-1099.39181535	-161.90882447	-151.25984753	-31.13608167	-26.81603535	-18.85346237	-4.81292425	-3.37420604	-1.00615152	-0.28009664	-0.034651269
53	-1144.95872041	-169.79608757	-158.87893701	-33.15920544	-28.69841162	-20.46929504	-5.30700485	-3.79792519	-1.28524929	-0.33010152	-0.049319259
54	-1191.47425451	-177.88824165	-166.70173403	-35.25187508	-30.64959710	-22.15303866	-5.82421316	-4.24371893	-1.58593153	-0.38102733	-0.065446657

Remark 45. *Our numerical simulations seem to show that for all* $1 \leq z \leq 54$*, there are no unoccupied negative eigenvalues in the rHF model.*

We end this section by the following figures, which back up the conjecture rHF atomic densities are strictly decreasing radial functions of the distance to the nucleus.

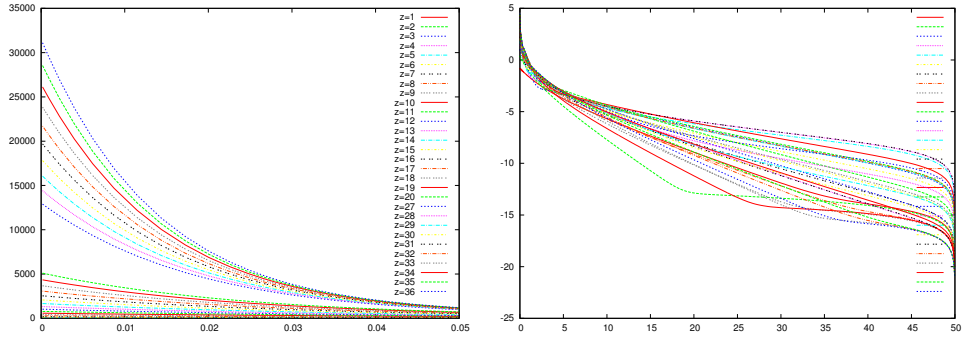


Figure 4.3 – The left figure is the plot of the densities of all the atoms $1 \leq z \leq 54$ with non-accidental degeneracy at the Fermi level, as a function of the distance to the nucleus, on the interval $[0, 0.05]$. The right one is the plot of the logarithms of those densities on the interval $[0, 50]$ (with $L_e = 50$.

Occupied energy levels in the Xα model

Recall that, in the Xα model, we have $v_{\mathrm{xc}}(\rho) = -(\frac{3}{\pi})^{\frac{1}{3}}\rho^{\frac{1}{3}}$ and $E_{\mathrm{xc}}(\rho) = -\frac{3}{4}\left(\frac{3}{\pi}\right)^{\frac{1}{3}}\int_{\mathbb{R}^3}\rho^{\frac{4}{3}}$, so that the exchange-correlation contributions must be computed by numerical quadratures. We use here the Gauss quadrature method with $N_{\mathrm{g},r} = 15$ and $N_{\mathrm{g},\theta} = 30$ (see Section 4.3.1). The tables below provide the negative eigenvalues of the Kohn-Sham Xα Hamiltonian for all the atoms of the first four rows of the periodic table. We observe that atoms z, with $23 \leq z \leq 28$ and $41 \leq z \leq 44$ have accidentally degenerate Fermi levels, the degeneracy occurring in all cases between an s-shell and a d-shell (4s-3d for $23 \leq z \leq 28$, 5s-4d for $41 \leq z \leq 44$) . All the results of this section are obtained for $L_e = 50$ and $N_I = 50$.

Hydrogen and Helium:

z	1s
1	-0.19425006
2	-0.51696819

First row:

z	1s	2s	2p
3	-1.82059688	-7.903269E-2	-0.01980414
4	-3.79318208	-0.17002882	-0.04568118
5	-6.50218508	-0.30537740	-0.10004190
6	-9.88411109	-0.45738266	-0.15795225
7	-13.94600837	-0.62884191	-0.22100492
8	-18.69081532	-0.82059960	-0.28951252
9	-24.12007582	-1.03296355	-0.36353478
10	-30.23473335	-1.26604957	-0.44305634

Second row:

z	1s	2s	2p	3s	3p
11	-37.64758180	-2.00773745	-1.00602899	-0.07701608	-
12	-45.89700050	-2.84556771	-1.66130099	-0.14212957	-
13	-55.08056245	-3.87797891	-2.50729361	-0.25134003	-0.07177562
14	-65.10729333	-5.01701318	-3.45670306	-0.35912165	-0.11781396
15	-75.98288074	-6.26974906	-4.51657129	-0.47007048	-0.16667495
16	-87.70907634	-7.63874114	-5.68939939	-0.58562735	-0.21887553
17	-100.2866151	-9.12522188	-6.97637829	-0.70643843	-0.27456776
18	-113.7158648	-10.7298831	-8.37817028	-0.83284590	-0.33379865

Third row:

z	1s	2s	2p	3s	3p	4s	3d
19	-128.33088855	-12.77542310	-10.21910630	-1.23313747	-0.64663669	-0.06446060	-
20	-143.84855797	-14.98113891	-12.21828949	-1.65584549	-0.98139181	-0.11135946	-
21	-160.10133445	-17.14580897	-14.17782407	-1.94114079	-1.18677960	-0.12562079	-0.08993616
22	-177.19446604	-19.39840741	-16.22419871	-2.21070037	-1.37630293	-0.13516712	-0.12742135

z	1s	2s	2p	3s	3p	4s	3d	t_0 on 4s
23	-195.11079	-21.72028	-18.33888	-2.44810	-1.53340	-0.13684	-0.13684	1.80348
24	-213.87746	-24.14440	-20.55424	-2.68033	-1.68342	-0.13575	-0.13575	1.56344
25	-233.50874	-26.68762	-22.88689	-2.92165	-1.83995	-0.13474	-0.13474	1.36094
26	-254.00468	-29.35014	-25.33699	-3.17214	-2.00304	-0.13379	-0.13379	1.18853
27	-275.36533	-32.13213	-27.90468	-3.43191	-2.17274	-0.13292	-0.13292	1.04052
28	-297.59072	-35.03373	-30.59009	-3.70102	-2.34907	-0.13212	-0.13212	0.91251

z	1s	2s	2p	3s	3p	3d	4s	4p
29	-320.71113046	-38.08838872	-33.42631684	-4.01075021	-2.56269325	-0.15772095	-0.13853326	-
30	-344.88588666	-41.47118261	-36.58668322	-4.51985307	-2.96945715	-0.34823478	-0.18536698	-
31	-370.08694818	-45.14035375	-40.03094135	-5.18870626	-3.53208119	-0.68572747	-0.29087281	-0.07062410
32	-396.20670224	-48.99180349	-43.65480075	-5.90610365	-4.13981877	-1.06418169	-0.38678393	-0.11469598
33	-423.24795332	-53.02694591	-47.45990056	-6.67318606	-4.79450154	-1.48714865	-0.48133889	-0.15888526
34	-451.20940700	-57.24351130	-51.44413418	-7.48771399	-5.49435363	-1.95357905	-0.57651339	-0.20426009
35	-480.08984982	-61.63957319	-55.60570006	-8.34791183	-6.23792096	-2.46234253	-0.67311692	-0.25119926
36	-509.88839450	-66.21370906	-59.94327472	-9.25254377	-7.02419663	-3.01257433	-0.77157332	-0.29987488

Fourth row:

z	1s	2s	2p	3s	3p	3d	4s	4p	5s	4d
37	-540.86299141	-71.21967003	-64.71130538	-10.45230037	-8.10401360	-3.85483317	-1.08806572	-0.54736605	-0.06148775	-
38	-572.77371002	-76.41823515	-69.67048854	-11.70829319	-9.23867588	-4.75086849	-1.40702066	-0.79807906	-0.10273762	-
39	-605.53830731	-81.71901613	-74.73119930	-12.93252908	-10.34028964	-5.61229300	-1.65169456	-0.98042181	-0.12072164	-0.07191940
40	-639.19811617	-87.16714952	-79.93818365	-14.17103753	-11.45501932	-6.48554899	-1.87316127	-1.14187376	-0.13103765	-0.11153445

z	1s	2s	2p	3s	3p	3d	4s	4p	5s	4d	t_0 on 5s
41	-673.73	-92.74	-85.27	-15.40	-12.56	-7.35	-2.05	-1.27	-0.131	-0.131	0.43
42	-709.14	-98.44	-90.72	-16.63	-13.66	-8.20	-2.19	-1.35	-0.11	-0.11	0.49
43	-745.47	-104.31	-96.35	-17.90	-14.80	-9.10	-2.34	-1.43	-0.106	-0.106	0.52
44	-782.72	-110.36	-102.15	-19.20	-15.98	-10.03	-2.482	-1.52	-0.091	-0.091	1.58

z	1s	2s	2p	3s	3p	3d	4s	4p	4d	5s	5p
45	-820.92037210	-116.61462706	-108.16375469	-20.58519414	-17.23463593	-11.03598845	-2.66114841	-1.64573152	-0.10328896	-	-
46	-860.04005143	-123.04183023	-114.34293438	-22.00846063	-18.52807961	-12.07926430	-2.84546201	-1.77155380	-0.11897024	-	-
47	-900.22199578	-129.79046984	-120.84193123	-23.62015666	-20.00902516	-13.30887072	-3.17386649	-2.03765069	-0.25210378	-0.12413645	-
48	-941.36800831	-136.75927851	-127.55983800	-25.31799286	-21.57523963	-14.62254311	-3.54347710	-2.34306170	-0.42072334	-0.16782523	-
49	-983.53661310	-144.00564974	-134.55408885	-27.15937608	-23.28414797	-16.07767931	-4.01092920	-2.74459266	-0.68157835	-0.25392457	-0.07116224
50	-1026.64612079	-151.44937883	-141.74444883	-29.06302510	-25.05452546	-17.59329598	-4.49305138	-3.15921725	-0.95435554	-0.33058463	-0.11021256
51	-1070.70153266	-159.09520245	-149.13571744	-31.03355268	-26.89101534	-19.17406284	-4.99473289	-3.59218268	-1.24495452	-0.40462751	-0.14839056
52	-1115.70333560	-166.94345654	-156.72827917	-33.07120441	-28.79389045	-20.82027875	-5.51644865	-4.04419106	-1.55433179	-0.47795434	-0.18678349
53	-1161.65132530	-174.99385350	-164.52188686	-35.17562866	-30.76282361	-22.53163992	-6.05805748	-4.51525592	-1.88259825	-0.55138448	-0.22581410
54	-1208.54517097	-183.24602834	-172.51621060	-37.34641486	-32.79742631	-24.30777853	-6.61934032	-5.00526767	-2.22967177	-0.62535460	-0.26568953

4.4.2 Perturbation by a uniform electric field (Stark effect)

In this section, we consider atoms subjected to a uniform electric field, that is to an external potential βW_{Stark} with

$$W_{\text{Stark}}(\mathbf{r}) = -e_{\mathbf{z}} \cdot \mathbf{r},$$

or, in spherical coordinates,

$$W_{\text{Stark}}(r, \theta, \varphi) = -\sqrt{\frac{4\pi}{3}} r Y_1^0(\theta, \varphi).$$

As already mentioned in Section 4.2.2, $\widetilde{\mathcal{I}}_{z,N}^{\text{rHF/LDA}}(\beta W_{\text{Stark}}) = -\infty$ whenever $\beta \neq 0$, and the corresponding variational problem has no minimizer. However, one can find a minimizer $\gamma_h \in \mathcal{K}_{N,h}$ to the approximated problem $\widetilde{\mathcal{I}}_{z,N,h}^{\text{rHF/LDA}}(\beta W_{\text{Stark}})$. The following figures are

the plot in the xy-plane of the density ρ_h multiplied by $|\mathbf{r}|^2$ for the boron atom ($z = 4$) obtained for different values of β:

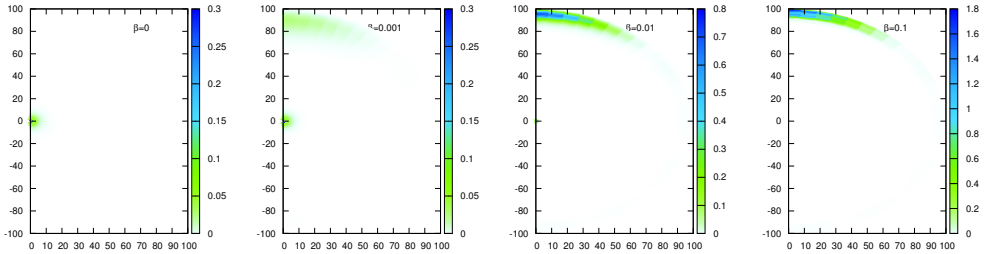


Figure 4.4 – rHF case: the left figure is a plot of the density of an isolated boron atom. The other ones are plots of the density of the boron atom subjected to a uniform external electric field, with coupling constants $\beta = 10^{-3}, 10^{-2}, 10^{-1}$, respectively.

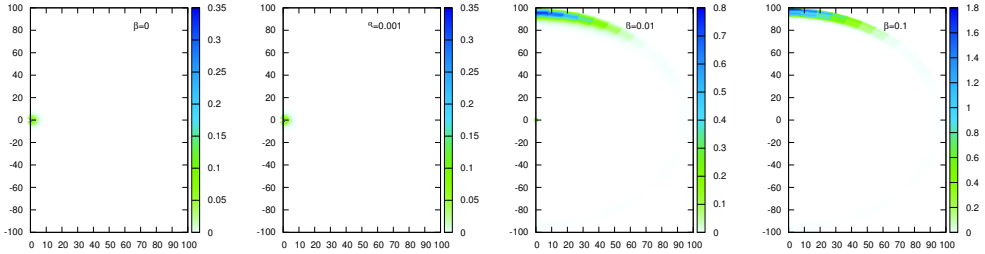


Figure 4.5 – Xα case: The first figure is a plot of the density of an isolated boron atom. The other ones are plots the density of the boron atom subjected to a uniform external electric field, with coupling constants $\beta = 10^{-3}, 10^{-2}, 10^{-1}$, respectively.

For $\beta = 10^{-2}$ and $\beta = 10^{-1}$, we clearly see boundary effects: part of the electronic cloud is localized in the region where the external potential takes highly negative values. This result is obviously not physical. On the other hand, for the Xα model and for $\beta = 10^{-3}$ we simply observe a polarization of the electronic cloud. The perturbation potential being not spherically symmetric, it breaks the symmetry of the density. This numerical solution can probably be interpreted as a (nonlinear) resonant state. We will come back to the analysis of this interesting case in a following work.

Fig. 4.6 shows the amount of electrons in the boron atom which escape to infinity as a function of the coupling constant β (for $L_e = 100$), in the rHF case.

While $\widetilde{\mathcal{I}}^{\mathrm{rHF/LDA}}_{z,N}(\beta W_{\mathrm{Stark}}) = -\infty$ and the corresponding variational problem has no minimizer, the first-order perturbation $\gamma^{(1),\mathrm{rHF}}_{z,N,W_{\mathrm{Stark}}}$ of the ground state density matrix does exist (see Theorem 43). If we consider the boron atom, it can be expressed as a function of the unperturbed occupied Kohn-Sham orbitals and of their first-order perturbations. We indeed have

$$\gamma^{(1),\mathrm{rHF}}_{4,4,W_{\mathrm{Stark}}} = \sum_{(m,k)\in\mathcal{O}_{4,4}} 2|\Phi^{(0)}_{m,k}\rangle\langle\Phi^{(1)}_{m,k}| + 2|\Phi^{(1)}_{m,k}\rangle\langle\Phi^{(0)}_{m,k}|,$$

where $\mathcal{O}_{4,4} = \{(0,1),(0,2)\}$, where $\epsilon^{(0)}_{m,k}$ is the k-th lowest eigenvalue of $H^{0,\mathrm{rHF}}_{4,4}$ in the

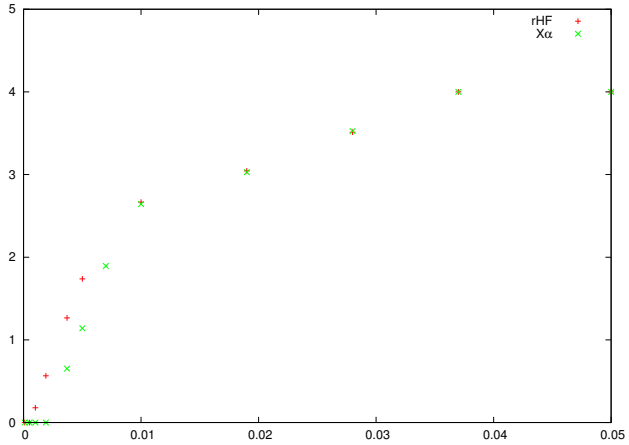


Figure 4.6 – The plot of the integral on $B_{100} \setminus B_{50}$ of the density ρ_h for $L_e = 100$ as a function of β in the rHF and Xα case.

subspace $\mathcal{H}^m$ and $\Phi^{(0)}_{m,k}$ an associated normalized eigenfunction, while $\epsilon^{(1)}_{m,k}$ and $\Phi^{(1)}_{m,k}$ satisfy the following self-consistent equation

$$\left(H^{0,\mathrm{rHF}}_{4,4} - \epsilon^{(0)}_{m,k}\right)\Phi^{(1)}_{m,k} + 2\left(\sum_{(m',k')\in\mathcal{O}_{4,4}} 2\Phi^{(0)}_{m',k'}\Phi^{(1)}_{m',k'} \star |\cdot|^{-1}\right)\Phi^{(0)}_{m,k} + W_{\mathrm{Stark}}\Phi^{(0)}_{m,k} = \epsilon^{(1)}_{m,k}\Phi^{(0)}_{m,k},$$

$$\int_{\mathbb{R}^3} \Phi^{(1)}_{m,k}\Phi^{(0)}_{m,k} = 0.$$

We denote by $\epsilon^{(0)}_{h,m,k}, \epsilon^{(1)}_{h,m,k}, \Phi^{(0)}_{h,m,k}$ and $\Phi^{(1)}_{h,m,k}$ the approximations of $\epsilon^{(0)}_{m,k}, \epsilon^{(1)}_{m,k}, \Phi^{(0)}_{m,k}$ and $\Phi^{(1)}_{m,k}$. For each $(m,k) \in \mathcal{O}_{4,4}$, define

$$\widetilde{\Phi}^{(1)}_{h,m,k}(\beta) := \frac{1}{\beta}(\Phi_{h,m,k}(\beta) - \Phi^{(0)}_{h,m,k}).$$

Recall that, $(\Phi_{h,m,k}(\beta))_{(m,k)\in\mathcal{O}_{4,4}}$ are the eigenfunctions of the density matrix γ_h, the minimizer of the approximated problem $\widetilde{\mathcal{I}}^{\mathrm{rHF}}_{z,N,h}(\beta W_{\mathrm{Stark}})$.

Let $U^{m,k}$ and $\widetilde{U}^{m,k}(\beta)$ be such that

$$\Phi^{(0)}_{h,m,k}(r,\theta,\varphi) = \sum_{l=|m|}^{m_h}\left(\sum_{i=1}^{N_h} U^{m,k}_{i,l}(\beta)\mathcal{X}_i(r)/r\right)Y^m_l(\theta,\varphi) \quad \text{and}$$

$$\widetilde{\Phi}^{(1)}_{h,m,k}(\beta)(r,\theta,\varphi) = \sum_{l=|m|}^{m_h}\left(\sum_{i=1}^{N_h} \widetilde{U}^{m,k}_{i,l}(\beta)\mathcal{X}_i(r)/r\right)Y^m_l(\theta,\varphi).$$

To show that $\widetilde{\Phi}^{(1)}_{h,m,k}(\beta) \to \Phi^{(1)}_{h,m,k}$ when $\beta \to 0$, it is enough to show that for each $l \geq 0$

$$\left(\frac{1}{2}A + \frac{l(l+1)}{2}M_{-2} - zM_{-1} + NV_\mu - \epsilon^{(0)}M_0\right)\widetilde{U}_{.,l}(\beta) - \frac{1}{\sqrt{3}}C^{1,m}M_1U_{.,l-1} - \frac{1}{\sqrt{3}}C^{1,m}M_1U_{.,l+1}$$
$$+ \sum_{l'=|m|}^{m_h}\sum_{l''=0}^{2m_h} C^{l,m}_{l',l''}([Q_{l''}]^T \cdot F)\widetilde{U}_{.,l'}(\beta) + 2C^{l,m}_{l',l''}([\widetilde{Q}_{l''}(\beta)]^T \cdot F)U_{.,l'} - \epsilon^{(1)}M_0U_{.,l} \underset{\beta\to 0}{\to} 0. \tag{4.57}$$

The index (m,k) is omitted for simplicity and the vector $\widetilde{Q}_l(\beta)$ is the solution to the linear system

$$\left(A^{\mathrm{a}} + l(l+1)M^{\mathrm{a}}_{-2}\right)\widetilde{Q}_l = 4\pi F : \widetilde{R}_l,$$

with

$$\widetilde{R}_l := \sum_{\substack{-m_h\le m\le m_h \\ 1\le k\le (m_h-|m|+1)\times N_h}} 2\widetilde{U}^{m,k}C^{l,m}[\widetilde{U}^{m,k}]^T.$$

Our numerical results show that, as expected by symmetry, $\epsilon^{(1)}_{h,m,k} = 0$ for all $(m,k) \in \mathcal{O}_{4,4}$, and that the left-hand side of (4.57) converges to zero linearly in β.

Appendix: discretization with $\mathbb{P}4$ finite elements

In this appendix, we elaborate on the details of the calculation.

A1. Basis functions

We have chosen the following form functions to build the finite element matrices and tensors:

$$z_1(t) = 1-t, \quad z_2(t) = t, \quad z_3(t) = 4t(1-t) = -4t^2 + 4t,$$
$$z_4(t) = \frac{128}{3}t\left(\frac{1}{2}-t\right)\left(\frac{3}{4}-t\right)(1-t) = -\frac{128}{3}\left(t^4 - \frac{9}{4}t^3 + \frac{13}{8}t^2 - \frac{3}{8}t\right),$$
$$z_5(t) = \frac{128}{3}t\left(t-\frac{1}{4}\right)\left(t-\frac{1}{2}\right)(1-t) = -\frac{128}{3}\left(t^4 - \frac{7}{4}t^3 + \frac{7}{8}t^2 - \frac{1}{8}t\right).$$

Their derivatives are given by:

$$z_1'(t) = -1, \quad z_2'(t) = 1, \quad z_3'(t) = -8t + 4,$$
$$z_4'(t) = -\frac{128}{3}\left(4t^3 - \frac{27}{4}t^2 + \frac{13}{4}t - \frac{3}{8}\right), \quad z_5'(t) = -\frac{128}{3}\left(4t^3 - \frac{21}{4}t^2 + \frac{7}{4}t - \frac{1}{8}\right).$$

Finite element basis:

- the 1D Schrödinger equation is solved on the finite interval $[0, L_e]$ with zero Dirichlet boundary conditions
- the interval $[0, L_e]$ is decomposed in N_I intervals of positive lengths $h_1, \cdots h_{N_I}$. Let $0 = r_1 < r_2 < \cdots < r_{N_I} < r_{N_I+1} = L_e$ be such that $h_k = r_{k+1} - r_k$;

- we denote by

$$V_h = \left\{ v \in C^0([0, L_e]) \text{ s.t. } v|_{[r_k, r_{k+1}]} \in \mathbb{P}_4, \quad v(0) = v(L_e) = 0 \right\}$$

the $\mathbb{P}_4$ finite element space associated with the so-defined mesh. We have

$$\dim(V_h) = 4N_I - 1;$$

- we then set for all $1 \leq k \leq N_I$ and $1 \leq j \leq 5$,

$$p_j^k(r) = z_j\left(\frac{r - r_k}{h_k}\right)$$

so that $p_j^k(r_k + t h_k) = z_j(t)$, and define the basis $(\chi_1, \cdots, \chi_{4N_I-1})$ of V_h as follows:

$$\chi_1(r) = p_3^1(r)\mathbb{1}_{[r_1,r_2]}, \quad \chi_2(r) = p_4^1(r)\mathbb{1}_{[r_1,r_2]}, \quad \chi_3(r) = p_5^1(r)\mathbb{1}_{[r_1,r_2]},$$

and for all $2 \leq k \leq N_I$,

$$\left\{ \begin{array}{l} \chi_{4k-4}(r) = p_2^{k-1}(r)\mathbb{1}_{[r_{k-1},r_k]} + p_1^k(r)\mathbb{1}_{[r_k,r_{k+1}]} \\ \chi_{4k-3}(r) = p_3^k(r)\mathbb{1}_{[r_k,r_{k+1}]} \\ \chi_{4k-2}(r) = p_4^k(r)\mathbb{1}_{[r_k,r_{k+1}]} \\ \chi_{4k-1}(r) = p_5^k(r)\mathbb{1}_{[r_k,r_{k+1}]}. \end{array} \right.$$

A2. Assembling the matrices

Let Λ be the bijective mapping from $\{0,1,2,3,4\}$ to $\{1,2,3,4,5\}$ defined by

$$\Lambda(0) = 2, \quad \Lambda(1) = 5, \quad \Lambda(2) = 4, \quad \Lambda(3) = 3, \quad \text{and} \quad \Lambda(4) = 1.$$

Recall that the density is equal to

$$\rho_h(r,\theta) = \sum_{l=0}^{2m_h} \sum_{i,j=1}^{N_h} [R_l]_{i,j} \frac{\mathcal{X}_i(r)}{r} \frac{\mathcal{X}_j(r)}{r} Y_l^0(\theta).$$

Using the finite element basis defined above, one gets that $\rho_h(r,\theta)$ is equal to

$$\left| \begin{array}{ll} \sum_{l=0}^{2m_h} \sum_{i,j=0}^{3} [R_l]_{4-i,4-j} \frac{p^1_{\Lambda(i)}(r)}{r} \frac{p^1_{\Lambda(j)}(r)}{r} Y_l^0(\theta) & \text{if} \quad r \in (r_1, r_2) \\ \sum_{l=0}^{2m_h} \sum_{i,j=0}^{4} [R_l]_{4k-i,4k-j} \frac{p^k_{\Lambda(i)}(r)}{r} \frac{p^k_{\Lambda(j)}(r)}{r} Y_l^0(\theta) & \text{if} \quad r \in (r_k, r_{k+1}), \quad 1 < k < N_I \\ \sum_{l=0}^{2m_h} \sum_{i,j=1}^{4} [R_l]_{4N_I-i,4N_I-j} \frac{p^{N_I}_{\Lambda(i)}(r)}{r} \frac{p^{N_I}_{\Lambda(j)}(r)}{r} Y_l^0(\theta) & \text{if} \quad r \in (r_{N_I}, r_{N_I+1}). \end{array} \right.$$

In particular, for $0 < t_{p,\mathrm{r}} < 1$ and $-1 < t_{q,\theta} < 1$, we have that $(t_{p,\mathrm{r}} h_k + r_k)^2 \rho(t_{p,\mathrm{r}} h_k + r_k, \arccos(t_{q,\theta}))$ is equal to

$$\left| \begin{array}{ll} \sum_{l=0}^{2m_h} \sum_{i,j=0}^{3} [R_l]_{4-i,4-j} z_{\Lambda(i)}(t_{p,\mathrm{r}}) z_{\Lambda(j)}(t_{p,\mathrm{r}}) \sqrt{\frac{2l+1}{4\pi}} P_l(t_{q,\theta}) & \text{if} \quad k = 1 \\ \sum_{l=0}^{2m_h} \sum_{i,j=0}^{4} [R_l]_{4k-i,4k-j} z_{\Lambda(i)}(t_{p,\mathrm{r}}) z_{\Lambda(j)}(t_{p,\mathrm{r}}) \sqrt{\frac{2l+1}{4\pi}} P_l(t_{q,\theta}) & \text{if} \quad 1 < k < N_I \\ \sum_{l=0}^{2m_h} \sum_{i,j=1}^{4} [R_l]_{4N_I-i,4N_I-j} z_{\Lambda(i)}(t_{p,\mathrm{r}}) z_{\Lambda(j)}(t_{p,\mathrm{r}}) \sqrt{\frac{2l+1}{4\pi}} P_l(t_{q,\theta}) & \text{if} \quad k = N_I, \end{array} \right. \quad (4.58)$$

where P_l are the Legendre polynomials, which can be calculated using the recurrence relation

$$P_n(x) = \frac{2n-1}{n} x P_{n-1}(x) - \frac{n-1}{n} P_{n-2}(x), \quad n \geq 2,$$

with $P_0(x) = 1$ and $P_1(x) = x$.

For $\mu(r\mathbf{e}) = \frac{\eta^2}{4\pi} \frac{e^{-\eta r}}{r}$, then

$$[V^{\mathrm{H}}(\mu)](r\mathbf{e}) = \frac{1}{r} \left(1 - e^{-\eta r}\right).$$

Thus the vector G in (4.43) has the following form

$$G = \left[g_3^1, g_4^1, g_5^1, \cdots, g_2^{k-1} + g_1^k, g_3^k, g_4^k, g_5^k, \cdots, g_2^{N_I - 1} + g_1^{N_I}, g_3^{N_I}, g_4^{N_I}, g_5^{N_I} \right]^T,$$

where

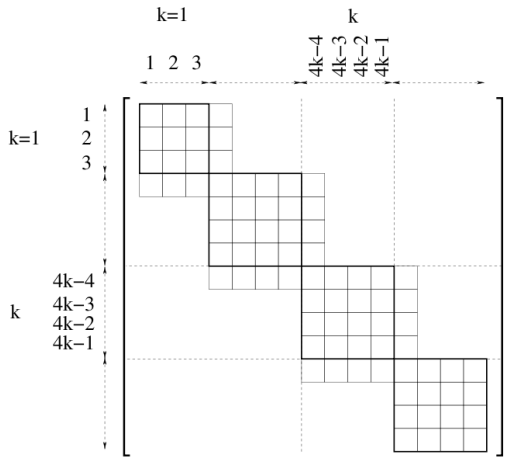
$$g_i^k = \frac{\eta^2}{4\pi} h_k e^{-\eta r_k} \int_0^1 e^{-\eta t h_k} z_i(t)\, dt.$$

We denote by

$$[\hat{\mathcal{H}}_{l,l'}] = \sum_{l''=0}^{2m_h} C_{l',l''}^{l,m} \left([Q_{l''}]^T \cdot F \right), \tag{4.59}$$

where $C^{l,m}$, Q_l and F are defined by (4.32), (4.40) and (4.42), respectively.

All the matrices A, M_{-2}, M_{-1}, M_0, M_1, V_μ, $[V_{\mathrm{xc}}^l]$ and $[\hat{\mathcal{H}}_{l,l'}]$ defined in (4.25), (4.35), (4.59) and (4.46) are symmetric and have the same pattern:



Their entries can be computed using elementary assembling matrices:

- diagonal blocks: for any $2 \leq k \leq N_I$, and any $1 \leq i \leq 4$ such that $1 \leq 4k-i \leq 4N_I-1$

$$\begin{array}{llll} Y_{4k-4,4k-4} = y^{k-1}_{22} + y^k_{11} & Y_{4k-4,4k-3} = y^k_{13} & Y_{4k-4,4k-2} = y^k_{14} & Y_{4k-4,4k-1} = y^k_{15} \\ Y_{4k-3,4k-4} = y^k_{31} & Y_{4k-3,4k-3} = y^k_{33} & Y_{4k-3,4k-2} = y^k_{34} & Y_{4k-3,4k-1} = y^k_{35} \\ Y_{4k-2,4k-4} = y^k_{41} & Y_{4k-2,4k-3} = y^k_{43} & Y_{4k-2,4k-2} = y^k_{44} & Y_{4k-2,4k-1} = y^k_{45} \\ Y_{4k-1,4k-4} = y^k_{51} & Y_{4k-1,4k-3} = y^k_{53} & Y_{4k-1,4k-2} = y^k_{54} & Y_{4k-1,4k-1} = y^k_{55} \end{array}$$

- off-diagonal blocks

$$Y_{4k-4,4k} = y^k_{12},\ Y_{4k-3,4k} = y^k_{23},\ Y_{4k-2,4k} = y^k_{24},\ Y_{4k-1,4k} = y^k_{25},$$

$$Y_{4k,4k-4} = y^k_{21},\ Y_{4k,4k-3} = y^k_{32},\ Y_{4k,4k-2} = y^k_{42},\ Y_{4k,4k-1} = y^k_{52}.$$

The y^k_{ij}'s are the entries of the elementary assembling matrices. The latter are defined for the matrices A, M_{-2}, M_{-1}, M_0, M_1, V_μ, $[V^l_{\rm xc}]$ and $[\hat{\mathcal{H}}_{l,l'}]$ as follows

$$\begin{aligned}
a^k_{ij} &= \int_{r_k}^{r_{k+1}} p^{k\prime}_i p^{k\prime}_j = h_k^{-1} \int_0^1 z'_i z'_j = h_k^{-1} \alpha_{ij} \\
(m_{-2})^k_{ij} &= \int_{r_k}^{r_{k+1}} \frac{p^k_i(r) p^k_j(r)}{r^2}\, dr = h_k \int_0^1 \frac{z_i(t) z_j(t)}{(r_k + t h_k)^2}\, dt \\
&= \left| \begin{array}{ll} h_k r_k^{-2} \int_0^1 \frac{z_i(t) z_j(t)}{(1+t h_k/r_k)^2}\, dt & \text{if } k \geq 2 \\ h_1^{-1} \int_0^1 \frac{z_i(t) z_j(t)}{t^2}\, dt & \text{if } k = 1 \end{array} \right. \\
(m_{-1})^k_{ij} &= \int_{r_k}^{r_{k+1}} \frac{p^k_i(r) p^k_j(r)}{r}\, dr = h_k \int_0^1 \frac{z_i(t) z_j(t)}{r_k + t h_k}\, dt \\
&= \left| \begin{array}{ll} h_k r_k^{-1} \int_0^1 \frac{z_i(t) z_j(t)}{1+t h_k/r_k}\, dt & \text{if } k \geq 2 \\ \int_0^1 \frac{z_i(t) z_j(t)}{t}\, dt & \text{if } k = 1 \end{array} \right. \\
(m_0)^k_{ij} &= \int_{r_k}^{r_{k+1}} p^k_i(r) p^k_j(r) dr = h_k \int_0^1 z_i(t) z_j(t) dt = h_k\, \nu_{ij} \\
(m_1)^k_{ij} &= \int_{r_k}^{r_{k+1}} r p^k_i(r) p^k_j(r) dr = h_k^2 \int_0^1 t z_i(t) z_j(t) dt + h_k r_k\, \nu_{ij} = h_k^2 \beta_{ij} + h_k r_k\, \nu_{ij} \\
(v_\mu)^k_{ij} &= (m_{-1})^k_{ij} - h_k e^{-\eta r_k} \int_0^1 \frac{e^{-\eta t h_k}}{r_k + t h_k} z_i(t) z_j(t)\, dt \\
&= \left| \begin{array}{ll} (m_{-1})^k - h_k r_k^{-1} e^{-\eta r_k} \int_0^1 \frac{e^{-\eta t h_k}}{1+t h_k/r_k} z_i(t) z_j(t)\, dt & \text{if } k \geq 2 \\ (m_{-1})^k - e^{-\eta r_k} \int_0^1 \frac{e^{-\eta t h_k}}{t} z_i(t) z_j(t)\, dt & \text{if } k = 1 \end{array} \right.
\end{aligned}$$

$$
\begin{aligned}
(v_{\mathrm{xc}}^{l})_{ij}^{k} &= c_{\mathrm{xc}} h_k \sqrt{\frac{2l+1}{4\pi}} \sum_{p=1}^{N_{g,\mathrm{r}}} \sum_{q=1}^{N_{g,\theta}} \omega_p \omega_q' \left(\rho(t_{p,\mathrm{r}} h_k + r_k, \arccos(t_{q,\theta}))\right)^{\frac{1}{3}} P_l(t_{q,\theta}) z_i(t_{p,\mathrm{r}}) z_j(t_{p,\mathrm{r}}) \\
&= c_{\mathrm{xc}} \left| \begin{array}{r} h_k r_k^{-1} \sqrt{\frac{2l+1}{4\pi}} \sum_{p=1}^{N_{g,\mathrm{r}}} \sum_{q=1}^{N_{g,\theta}} \omega_p \omega_q' \left((t_{p,\mathrm{r}} h_k + r_k)^2 \rho(t_{p,\mathrm{r}} h_k + r_k, \arccos(t_{q,\theta}))\right)^{\frac{1}{3}} \\ P_l(t_{q,\theta}) \frac{z_i(t_{p,\mathrm{r}}) z_j(t_{p,\mathrm{r}})}{t_{p,\mathrm{r}} h_k / r_k + 1} (t_{p,\mathrm{r}} h_k + r_k)^{\frac{1}{3}} \quad \text{if } k \geq 2 \\ \sqrt{\frac{2l+1}{4\pi}} \sum_{p=1}^{N_{g,\mathrm{r}}} \sum_{q=1}^{N_{g,\theta}} \omega_p \omega_q' \left((t_{p,\mathrm{r}} h_k)^2 \rho(t_{p,\mathrm{r}} h_k + r_k, \arccos(t_{q,\theta}))\right)^{\frac{1}{3}} \\ P_l(t_{q,\theta}) \frac{z_i(t_{p,\mathrm{r}}) z_j(t_{p,\mathrm{r}})}{t_{p,\mathrm{r}}} (t_{p,\mathrm{r}} h_k)^{\frac{1}{3}} \quad \text{if } k = 1 \end{array} \right.
\end{aligned}
$$

in the Xα-case, that is $v_{\mathrm{xc}}(\rho) = -(\frac{3}{\pi})^{\frac{1}{3}} \rho^{\frac{1}{3}}$,

$$
(\hat{h}_{l,l'})_{ij}^{k} = \left| \begin{array}{ll} \sum_{l''=0}^{2m_h} \sum_{n=1}^{3} c_{l,l',l''}^{m} f_{ij\Lambda(n)}^{k} Q_{l'',4-n} & \text{if } k = 1 \\ \sum_{l''=0}^{2m_h} \sum_{n=0}^{4} c_{l,l',l''}^{m} f_{ij\Lambda(n)}^{k} Q_{l'',4k-n} & \text{if } 1 < k < N_I \\ \sum_{l''=0}^{2m_h} \sum_{n=1}^{4} c_{l,l',l''}^{m} f_{ij\Lambda(n)}^{k} Q_{l'',4N_I-n} & \text{if } k = N_I, \end{array} \right.
$$

where

$$
f_{ijn}^{k} = \int_{r_k}^{r_{k+1}} \frac{p_i^k(r) p_j^k(r) p_n^k(r)}{r} dr = h_k \int_0^1 \frac{z_i(t) z_j(t) z_n(t)}{(t h_k + r_k)} dt,
$$

and

$$
c_{\mathrm{xc}} = -\sqrt{\pi} (\frac{3}{\pi})^{\frac{1}{3}}.
$$

Note that $\rho(t_{p,\mathrm{r}} h_k + r_k, \arccos(t_{q,\theta}))$ will be calculated with the help of (4.58). In addition to assembling the matrices, we need to deal with the following term

$$
\sum_{i,j=1}^{N_h} F_{ijn} [R_l]_{i,j}
$$

in order to calculate the right-hand side of (4.40). Let $k_n = 1 + \mathrm{int}(\frac{n}{4})$ and $q_n = 4 -$

$(n \bmod 4)$, so that $n = 4k_n - q_n$. Then $\sum_{i,j=1}^{N_h} F_{ijn}[R_l]_{i,j}$ is equal to

$$\begin{cases}
\sum_{i,j=0}^{3} h_1 f^1_{\Lambda(i)\Lambda(j)\Lambda(q_n)}[R_l]_{4-i,4-j} & \text{if} \quad k_n = 1 \\
\sum_{i,j=0}^{4} h_{k_n} f^{k_n}_{\Lambda(i)\Lambda(j)\Lambda(q_n)}[R_l]_{4k_n-i,4k_n-j} & \text{if} \quad q_n \neq 4 \quad \text{and} \quad 1 < k_n < N_I \\
\sum_{i,j=1}^{4} h_{k_{N_I}} f^{k_{N_I}}_{\Lambda(i)\Lambda(j)\Lambda(q_n)}[R_l]_{4k_{N_I}-i,4k_{N_I}-j} & \text{if} \quad q_n \neq 4 \quad \text{and} \quad k_n = N_I \\
\sum_{i,j=0}^{3} h_1 f^1_{2\Lambda(i)\Lambda(j)}[R_l]_{4-i,4-j} + \sum_{i,j=0}^{4} h_2 f^2_{1\Lambda(i)\Lambda(j)}[R_l]_{8-i,8-j} & \\
\qquad \text{if} \quad q_n = 4 \quad \text{and} \quad k = 2 & \\
\sum_{i,j=0}^{4} \Big[h_{k_n-1} f^{k_n-1}_{2\Lambda(i)\Lambda(j)}[R_l]_{4k_n-4-i,4k_n-4-j} & \\
\qquad \text{if} \quad q_n = 4 \quad \text{and} \quad 2 < k < N_I & \\
\qquad + h_{k_n} f^{k_n}_{1\Lambda(i)\Lambda(j)}[R_l]_{4k_n-i,4k_n-j} \Big] & \\
\sum_{i,j=0}^{4} h_{k_{N_I}-1} f^{k_{N_I}-1}_{2\Lambda(i)\Lambda(j)}[R_l]_{4k_{N_I}-4-i,4k_{N_I}-4-j} & \\
\qquad \text{if} \quad q_n = 4 \quad \text{and} \quad k = N_I. & \\
\quad + \sum_{i,j=1}^{4} h_{k_{N_I}} f^{k_{N_I}}_{1\Lambda(i)\Lambda(j)}[R_l]_{4k_{N_I}-i,4_{N_I}-j} &
\end{cases}$$

We end this section by providing the values of α_{ij}, β_{ij} and ν_{ij}, for $1 \leq i, j \leq 5$,

$$\begin{array}{lllll}
\alpha_{11} = 1 & \alpha_{12} = -1 & \alpha_{13} = 0 & \alpha_{14} = 0 & \alpha_{15} = 0 \\
\alpha_{21} = -1 & \alpha_{22} = 1 & \alpha_{23} = 0 & \alpha_{24} = 0 & \alpha_{25} = 0 \\
\alpha_{31} = 0 & \alpha_{32} = 0 & \alpha_{33} = 16/3 & \alpha_{34} = 128/45 & \alpha_{35} = 128/45 \\
\alpha_{41} = 0 & \alpha_{42} = 0 & \alpha_{43} = 128/45 & \alpha_{44} = 3328/189 & \alpha_{45} = 5888/945 \\
\alpha_{51} = 0 & \alpha_{52} = 0 & \alpha_{53} = 128/45 & \alpha_{54} = 5888/945 & \alpha_{55} = 3328/189
\end{array}$$

$$\begin{array}{lllll}
\nu_{11} = 1/3 & \nu_{12} = 1/6 & \nu_{13} = 1/3 & \nu_{14} = 4/15 & \nu_{15} = 4/45 \\
\nu_{21} = 1/6 & \nu_{22} = 1/3 & \nu_{23} = 1/3 & \nu_{24} = 4/45 & \nu_{25} = 4/15 \\
\nu_{31} = 1/3 & \nu_{32} = 1/3 & \nu_{33} = 8/15 & \nu_{34} = 64/315 & \nu_{35} = 64/315 \\
\nu_{41} = 4/15 & \nu_{42} = 4/45 & \nu_{43} = 64/315 & \nu_{44} = 128/405 & \nu_{45} = 128/2835 \\
\nu_{51} = 4/45 & \nu_{52} = 4/15 & \nu_{53} = 64/315 & \nu_{54} = 128/2835 & \nu_{55} = 128/405
\end{array}$$

$$\begin{array}{lllll}
\beta_{11} = 1/12 & \beta_{12} = 1/12 & \beta_{13} = 2/15 & \beta_{14} = 16/315 & \beta_{15} = 16/315 \\
\beta_{21} = 1/12 & \beta_{22} = 1/4 & \beta_{23} = 1/5 & \beta_{24} = 4/105 & \beta_{25} = 68/315 \\
\beta_{31} = 2/15 & \beta_{32} = 1/5 & \beta_{33} = 4/15 & \beta_{34} = 16/315 & \beta_{35} = 16/105 \\
\beta_{41} = 16/315 & \beta_{42} = 4/105 & \beta_{43} = 16/315 & \beta_{44} = 64/945 & \beta_{45} = 64/2835 \\
\beta_{51} = 332/105 & \beta_{52} = 1852/105 & \beta_{53} = 592/63 & \beta_{54} = 704/315 & \beta_{55} = 704/2835.
\end{array}$$

Appendix A

Spherical harmonics

The spherical harmonics are extensively used in basis functions in the computation of atomic orbital electron configuration. They were introduced as the joint eigenfunctions of L_z and L^2, in the spherical coordinates. The L_z is the generator of rotations about the azimuthal angle

$$L_z = -i\frac{\partial}{\partial\varphi}.$$

While, L^2 is the square of the orbital angular momentum operator $L = -ix \times \nabla$. That is,

$$L^2 = \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2(\theta)}\frac{\partial^2}{\partial\varphi^2},$$

known also by the Laplace-Beltrami operator, denoted by Δ_S. More precisely, we have

$$\Delta_S Y_l^m = -l(l+1)Y_l^m \quad \text{and} \quad -i\frac{\partial}{\partial\varphi}Y_l^m = mY_l^m,$$

where l is the angular momentum quantum number and m is the magnetic quantum number. There explicit expression is

$$Y_l^m(\theta,\varphi) = (-1)^m\sqrt{\frac{(2l+1)(l-m)!}{4\pi(l+m)!}}P_l^m(\cos\theta)e^{im\varphi}, \tag{A.1}$$

where P_l^m denotes the Legendre functions. The latter are obtained from the m-th derivative of the Legendre polynomials P_l, as follows: for $0 \le m \le l$

$$\begin{cases} P_l^m(\cos\theta) = (\sin\theta)^m\, P_l^{(m)}(\cos\theta) \\ P_l^{-m}(\cos\theta) = (-1)^m\frac{(l-m)!}{(l+m)!}P_l^{(m)}(\cos\theta). \end{cases}$$

The Legendre polynomials can be computed using the Rodrigues' formula:

$$P_l(x) = \frac{(-1)^l}{2^l l!}\frac{d^l}{dx^l}(1-x^2)^l.$$

Note that, the Legendre polynomials satisfy the following recurrence relation

$$P_n(x) = \frac{2n-1}{n}xP_{n-1}(x) - \frac{n-1}{n}P_{n-2}(x), \quad n \ge 2,$$

with $P_0(x) = 1$ and $P_1(x) = x$.

To fix the idea, the spherical harmonics for $l = 0, 1$ and 2 are given by

$$
\begin{aligned}
&Y_0^0(\theta,\varphi) = \tfrac{1}{2}\sqrt{\tfrac{1}{\pi}},\\
&Y_1^0(\theta,\varphi) = \tfrac{1}{2}\sqrt{\tfrac{3}{\pi}}\cos\theta, \quad Y_1^{\pm 1}(\theta,\varphi) = \mp\tfrac{1}{2}\sqrt{\tfrac{3}{2\pi}}\sin\theta\, e^{\pm i\varphi},\\
&Y_2^0(\theta,\varphi) = \tfrac{1}{4}\sqrt{\tfrac{5}{\pi}}(3\cos^2\theta - 1), \quad Y_2^{\pm 1}(\theta,\varphi) = \mp\tfrac{1}{2}\sqrt{\tfrac{15}{2\pi}}\sin\theta\,\cos\theta\, e^{\pm i\varphi},\\
&Y_2^{\pm 2}(\theta,\varphi) = \tfrac{1}{4}\sqrt{\tfrac{15}{2\pi}}\sin^2\theta\, e^{\pm 2i\varphi}.
\end{aligned}
$$

Properties of spherical harmonics

The spherical harmonics, given by (A.1), satisfy the following properties

- They are orthonormal functions, that is for $l \geq 0$, $-l \leq m \leq l$ and $l' \geq 0$, $-l' \leq m' \leq l'$, we have

$$\int_{\mathbb{S}^2} Y_l^m (Y_{l'}^{m'})^* = \int_0^{\pi}\int_0^{2\pi} Y_l^m(\theta,\varphi) Y_{l'}^{m'}(\theta,\varphi)^* \sin\theta\, d\varphi\, d\theta = \delta_{ll'}\delta_{mm'}$$

  where δ_{ij} is the Kronecker symbol, $\mathbb{S}^2$ is the unit sphere of $\mathbb{R}^3$, and $Y_l^m(\theta,\varphi)^* = (-1)^m Y_l^{-m}(\theta,\varphi)$.

- The set $\{Y_l^m\}_{l\geq 0, -l\leq m\leq l}$ form a basis of the Hilbert space $L^2(\mathbb{S}^2)$.

- Any $f \in L^2(\mathbb{S}^2)$ can be expressed uniquely as a linear combination of the spherical harmonics, as

$$f = \sum_{l\geq 0}\sum_{m=-l}^{m=l} \langle Y_l^m, f\rangle_{L^2(\mathbb{S}^2)} Y_l^m.$$

  The coefficients $\langle Y_l^m, f\rangle_{L^2(\mathbb{S}^2)} = \int_{\mathbb{S}^2} Y_l^m f$.

Furthermore, the spherical harmonics satisfy an addition theorem, which states

$$\sum_{m=-l}^{m=l} Y_l^m(\theta_1,\varphi_1) Y_l^m(\theta_2,\varphi_2)^* = \frac{2l+1}{4\pi} P_l(\cos\omega),$$

where ω describes the angle between two unit vectors oriented at the polar coordinates (θ_1,φ_1) and (θ_2,φ_2) with

$$\cos\omega = \cos\theta_1\,\cos\theta_2 + \sin\theta_1\,\sin\theta_2\,\cos(\varphi_1 - \varphi_2).$$

In particular, when $\theta_1 = \theta_2 = \theta$ and $\varphi_1 = \varphi_2 = \varphi$, gives the Unsöld's theorem [88]

$$\sum_{m=-l}^{m=l} Y_l^m(\theta,\varphi) Y_l^m(\theta,\varphi)^* = \frac{2l+1}{4\pi}.$$

Since the solutions of the non-relativistic Schrödinger equation can be made real, it is important to define the real forms of the spherical harmonics. Thus using these later functions, the programs don't need anymore to use complex algebra. Real spherical harmonics are defined from the complex ones by

$$\mathcal{Y}_l^m = \begin{cases} \frac{i}{\sqrt{2}}\left(Y_l^{-|m|} - (-1)^m Y_l^{|m|}\right) & \text{if} \quad m < 0 \\ Y_l^0 & \text{if} \quad m = 0 \\ \frac{1}{\sqrt{2}}\left(Y_l^{-|m|} + (-1)^m Y_l^{|m|}\right) & \text{if} \quad m > 0. \end{cases}$$

Graphical representation of spherical harmonics

The spherical harmonics are usually represented graphically. Here are two figures: first for some complex spherical harmonics, second for their linear combinations which correspond to the angular functions of orbitals.

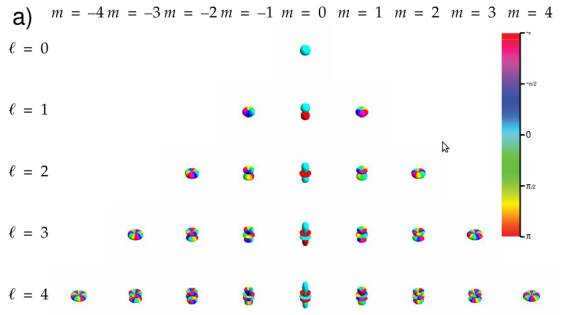


Figure A.1 – Plot of the spherical harmonics where the phase of the function is color coded.

Product of two spherical harmonics

The product of two spherical harmonics can be expressed in terms of spherical harmonics, since they form an orthonormal basis set. The product is written with the help of the Wigner 3j-symbols [15, 30], as follows

$$Y_{l_1}^{m_1} Y_{l_2}^{m_2} = \sum_{l_3=|l_1-l_2|}^{l=l_1+l_2} \sqrt{\frac{(2l_1+1)(2l_2+1)(2l_3+1)}{4\pi}} \begin{pmatrix} l_1 & l_2 & l_3 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_1 & l_2 & l_3 \\ m_1 & m_2 & -(m_1+m_2) \end{pmatrix} (Y_l^{m_1+m_2})^*.$$

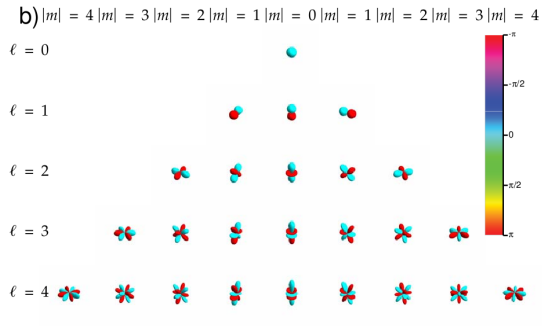


Figure A.2 – Plot of the real spherical harmonis, which are usually shown as the atomic orbitals.

The Wigner 3j-symbol $\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix}$ can be found in tables in books (see [73] for instance). It is related to the Clebsh-Gordan coefficients by

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} = (-1)^{j_1+j_2+j_3} \frac{1}{\sqrt{2j_3+1}} c(j_1, m_1, j_2, m_2, j_3, -m_3).$$

It is identically zero unless all these conditions are satisfied

- $m_1 + m_2 + m_3 = 0$,
- $j_1 + j_2 + j_3$ is an integer (or an even integer if $m_1 = m_2 = m_3 = 0$),
- $|m_i| \leq j_i$,
- $|j_1 - j_2| \leq j_3 \leq j_1 + j_2$.

We will give some useful properties of this symbol, which facilitate the calculations. We start with the symmetry properties: a Wigner 3j-symbol is invariant under an even permutation of its columns, i.e

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} = \begin{pmatrix} j_2 & j_3 & j_1 \\ m_2 & m_3 & m_1 \end{pmatrix} = \begin{pmatrix} j_3 & j_1 & j_2 \\ m_3 & m_1 & m_2 \end{pmatrix},$$

while an odd permutation of the columns gives a phase factor

$$\begin{aligned} \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} &= (-1)^{j_1+j_2+j_3} \begin{pmatrix} j_2 & j_1 & j_3 \\ m_2 & m_1 & m_3 \end{pmatrix} \\ &= (-1)^{j_1+j_2+j_3} \begin{pmatrix} j_1 & j_3 & j_2 \\ m_1 & m_3 & m_2 \end{pmatrix}. \end{aligned}$$

The change of the sign of the m quantum numbers also gives a phase factor

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ -m_1 & -m_2 & -m_3 \end{pmatrix} = (-1)^{j_1+j_2+j_3} \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix}.$$

Moreover, let us note that these symbols satisfy the following important orthogonality relations

$$(2j+1) \sum_{m_1 m_2} \begin{pmatrix} j_1 & j_2 & j \\ m_1 & m_2 & m \end{pmatrix} \begin{pmatrix} j_1 & j_2 & j' \\ m_1 & m_2 & m' \end{pmatrix} = \delta_{jj'} \delta_{mm'},$$

and

$$\sum_{jm}(2j+1)\begin{pmatrix} j_1 & j_2 & j \\ m_1 & m_2 & m \end{pmatrix}\begin{pmatrix} j_1 & j_2 & j \\ m_1' & m_2' & m \end{pmatrix} = \delta_{m_1 m_1'}\delta_{m_2 m_2'}.$$

The integration of the product of three spherical harmonics can be simplified using the product rule and the orthogonality condition. This leads to

$$\begin{aligned}\int_0^{\pi}\int_0^{2\pi} Y_{l_1}^{m_1}(\theta,\varphi)Y_{l_2}^{m_2}(\theta,\varphi)Y_{l_3}^{m_3}(\theta,\varphi)\sin\theta\,d\varphi\,d\theta \\ = \sqrt{\frac{(2l_1+1)(2l_2+1)(2l_3+1)}{4\pi}}\begin{pmatrix} l_1 & l_2 & l_3 \\ 0 & 0 & 0 \end{pmatrix} \\ \begin{pmatrix} l_1 & l_2 & l_3 \\ m_1 & m_2 & m_3 \end{pmatrix}.\end{aligned}$$

For the formulas stated in this appendix, we refer for instance to the following references [15, 30, 72].

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